GRAVIMETRIC ANALYSIS

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GRAVIMETRIC ANALYSIS

A LABORATORY MANUAL
WITH SPECIAL REFERENCE TO THE ANALYSIS OF NATURAL MINERALS AND ROCKS

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PREFACE.

The choice of the various analytical procedures given in this short manual is founded on my experience with the analysis of a large number of rocks and minerals. As indeed all substances under investigation in scientific and industrial research have their final origin in the earth's crust and as the presentation of the methods is so made as to include the analysis of the majority of other materials also, I venture to hope that this selection may be of use to students of analytical chemistry.

With regard to the choice of the methods here described, I wish to remark, that in some cases — though there is perhaps little or no preference for any particular one of two or more available methods — not all of these have been given to avoid overburdening the book. I have tried to mention methods which will most likely be applicable in the analysis of substances of widely differing composition whilst excluding those of more restricted importance. It need not be said that in particular cases viz. rapid analysis or simultaneous analysis of a large number of similar samples, in short for routine work, other procedures especially of a titrimetric nature may advantageously be used. These procedures are ordinarily known to the chemist working in industrial and commercial laboratories and may be found in the special literature on the subject. For convenience I have prepared a section with references to important citations in the text and an index which will I hope facilitate the choice of the analytical procedure to be employed. I shall feel under obligation if my attention is called to new methods or to improvements in the methods described.

I am indebted to Dr. L. C. Jackson of the Department of Physics, University of Bristol and to Mr. R. Wardell, Utrecht, who kindly revised the English MS. *). Mr. Wardell also assisted with the reading of the proofs. Lastly to D. B. Centen's Uitgevers-Maatschappij who made possible the publication of this book.

Utrecht, Mineralogical-Geological Institute of the State University.
October, 1936.

*) Dr. Jackson: p. 1—166.
Mr. Wardell: p. 167—236.

DIVISION OF THIS BOOK.

After the introduction there follows a description of common operations; then, complete procedures for the analysis of many natural substances are given under the following headings: 1. silicates, 2. other salts, 3. ores. In case of doubt concerning these three groups, the required information can be found in the index at the back of the book. Information is also given regarding the methods of analysis for any special element.

The references cited in the text are enumerated in a separate section at the end of the book. The reagents and solutions required for the methods described in this manual are listed in alphabetical order, the same with the necessary apparatus. This division has been purposely chosen, that the student may do all the preliminary work, viz. reading the whole description, when necessary, consulting the cited references, preparing the required solutions and apparatus before starting the analysis, thus avoiding many operative errors.

INTRODUCTION.

The division of this book is in harmony with the large geochemical unities of the earth and is consequently, strictly natural: elements behaving similarly in nature will most likely do the same in the laboratory.

Modern geochemical views are given in a condensed form in figures 1 and 2 and table I. Fig. 1 demonstrates the different layers in the earth, nickel-iron-core, sulphide-oxide-layer, eclogite layer (consisting of basic silicates with varying masses of sulphides and oxides), outer shell of less dense silicates, hydrosphere and atmosphere. These large subdivisions originated in a natural way in consequence of the amounts of the *quantitatively most important* elements, their chemical affinities and the action of the gravitational field. The *minor* elements are distributed over these layers according to their chemical affinities; this is expressed in table I. The weathering of the surface brought about the appearance of sedimentary rocks. Decomposition of silicates leads to sedimentation of difficultly soluble products (quartz, sesqui-oxides and clay-minerals) *in situ* or by mechanical transport, calcium and part of the magnesium are deposited mainly through biological action in the form of carbonate rocks and sometimes the more soluble salts are concentrated in the form of salt-beds (rest of calcium and magnesium, sodium and potassium with anions). This behaviour of

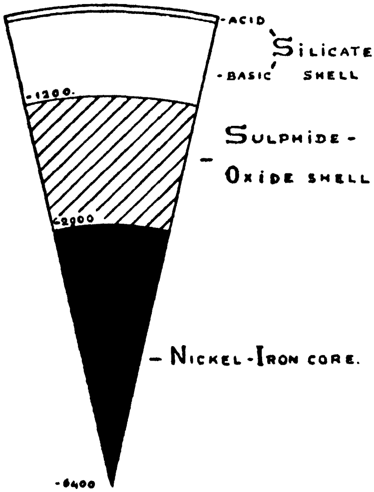

Fig. 1.

Geochemical Division of the Elements.

I.	II.	III.	IV.	V.
Iron, Siderophile.	Sulphur, Chalcophile.	Silicon, Lithophile.	Atmophile.	Biophile.
Fe, Ni, Co, P, (As), C, Ru, Rh. Pd. Os, Ir, Pt, Au. Ge. Sn. Mo, (W). (Nb), Ta.	(O), S, Se, Te, Fe, (Ni), (Co), Cu, Zn, Cd, Pb, Sn, Ge, Mo. As, Sb, Bi, Ag, (Au), Hg, Pd, Ru, (Pt). Ga, In, Tl.	O, (S), (P), (H), Si, Ti, Zr, Hf, Th, (Sn), F, Cl, Br, J. B, Al, (Ga), Sc, Y. La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tu, Yb, Cp. Li, Na, K, Rb, Cs. Be, Mg, Ca, Sr, Ba, (Fe), V, Cr, Mn, (Ni), (Co), Nb, Ta, W, U, (C).	H, N. C, (O), Cl, Br, J, He, Ne, Ar, Kr, Xe.	C, H. O. N, P, S, Cl, J, (B), (Ca, Mg, K, Na.) (V, Mn, Fe, Cu.)

Table I.

the elements in consequence of their ionic-potential is sketched in fig. 2. 1)

The differentiation and crystallisation of magmas is accom-

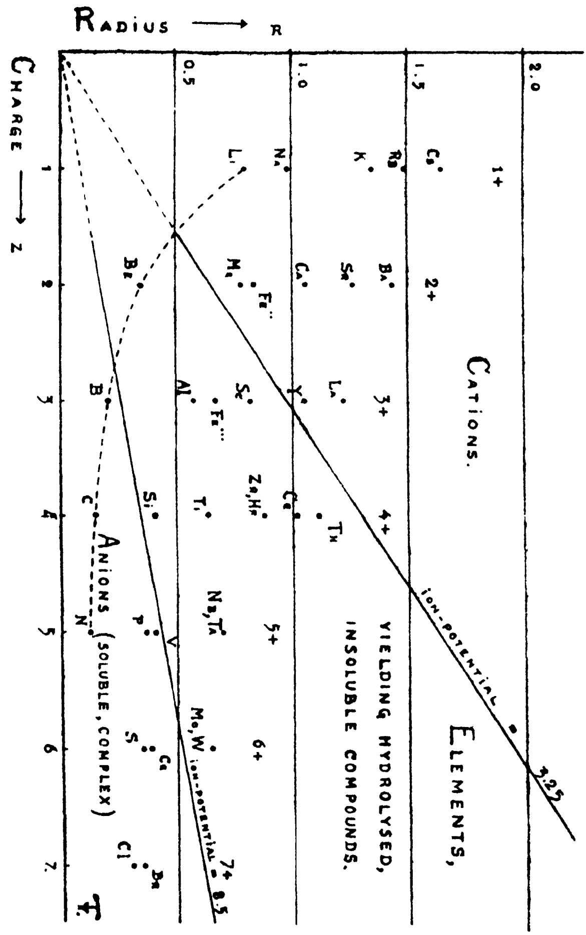

Fig. 2. Behaviour of the elements in consequence of their ionic-potential according to V. M. Goldschmidt.

panied by the segregration of relatively small amounts of ores (oxides and sulphides of heavy metals). These are concentrated in lodes and veins and furnish the raw-materials for metal-lurgical processes.

This book therefore treats the subject under the following groups:

	Silicate rocks and minerals Soils	ceramic raw-materials and products, building materials, cements, glasses, slags, coal- and plant-ash, etc.
	Sedimentary rocks: 1. quartz rocks, 2. clay-matter, 3. Fe-hydroxides, 4. Al-hydroxides, 5. carbonate rocks.	ceramic raw-materials and products, building materials, cements.
Natural minerals and rocks	Salt deposits and mineral waters: 1. carbonates, 2. sulphates, 3. phosphates, 4. halogen-salts, 5. borates, 6. nitrates, 7. iodates, chlorates, perchlorates, 8. mineral waters.	artificial manures, etc.
	Ore minerals: 1. oxides, 2. sulphides. 3. arsenic- and antimony-compounds.	 alloys. stones.
	Organic minerals and rocks	

Every group of natural minerals is followed by the artificial products similar in composition and these may be analysed consequently by the same methods. Ordinarily the natural products are much more complex, but some modern technical products, especially alloys, equal them in this respect.

In general a complete analysis consists of the following parts:

1. Devising a scheme for the analysis,
2. Preparation of the sample,
3. Execution of the analysis,
4. Calculation and discussion of the results.

These parts will be considered separately:

1. DEVISING A SCHEME FOR THE ANALYSIS.

The analysis of a substance containing a large number of elements is often a problem of great complexity. Due care should be taken, to plan an effective *scheme* for the execution of the analysis, thus avoiding unexpected complications of the work and finally saving much time. Even this complexity of many materials to be examined, suggests the application of gravimetric processes, as the precipitates, after having been weighed, can be easily inspected for contamination by foreign matter.

This part of the investigation already requires a knowledge of the constituents present in the substance. Even if not all of these are to be determined, the knowledge of the qualitative composition is indispensable to prevent any undesired constituent interfering with the determinations of the other elements. Some idea of the amounts of each element to be expected will also be very useful.

There are various ways of attacking this problem; which of these is to be applied depends largely on the nature of the material. In most technical examinations e.g. of alloys etc., the components are known and further search is not needed at all. To a certain degree this can also be said of rocks. In all other cases a qualitative examination should be made, to permit of planning a proper scheme for the quantitative analysis.

This part of the investigation may be made according to the well known principles of qualitative analysis and then preferably by microchemical or drop-reactions. [1a])

The spectrographic method is also capable of very general application. In one or two exposures one can easily get a review of all the metals and some of the non-metals present and rather definite statements as to the amount of each element can be made. For further particulars the literature on spectrum analysis should be consulted. [2]) In my opinion this method will gain more and more interest compared with the other methods of inorganic qualitative analysis.

In mineralogical researches some methods find application which may also be of value for chemists. Opaque minerals (ores, etc.) can easily be determined by blow-pipe methods. [3]) The methods of ore-microscopy of a metallographic nature

(examination with polarized light from polished surfaces) receive much attention nowadays and permit the detection of a certain mineral even if it is present in a very small amount.

The work is rather simple but one should have considerable experience with all the minerals in question and this method is likely to remain the territory of specialised mineralogists. [4]) Both these methods are succesfully applicable only to ores, the blow-pipe method also to several other groups of minerals but never to silicates. In general the non-opaque minerals are determined most conveniently by microscopical methods; the crystal-optical properties are examined and with a determination-table the mineral name is found. [5])

These mineralogical methods give valuable information about the minerals present, but in general the chemical composition cannot be computed from these data, most minerals having a considerable range of variation owing chiefly to isomorphous substitutions. Nevertheless it is very useful to have these particulars at one's disposal in planning the scheme for an analysis as they determine which elements should be looked for and to what amount each is to be expected.

It is the principle of isomorphism which governs the substitution of some elements by others in crystals. V. M. GOLDSCHMIDT has demonstrated in a number of extremely interesting publications on geochemistry that isomorphous substitution is related to the space required by an element in the crystal-lattice: "Der Krystall wägt seine Bestandteile nicht, sondern ordnet sie nach ihrem Raumbedarf". This proved to be the key, not only for the solution of a number of problems in geochemistry; analysis as well already profited much from these views. The main constituents of a given mineral being known from earlier analyses, [6]) these considerations fix our attention on minor constituents which should be determined, whilst another important result is, that we are now able to predict elements that are likely to be co-precipitated with other elements. So an enquiry in manuals on mineral chemistry for the elements which have already been found in minerals is best followed by a consideration of the hitherto unreported elements. It is for this purpose that fig. 3 has been prepared. *) This figure shows the

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*) NH_4^+ = 1.43 A. Z.A. = Rare Earths.

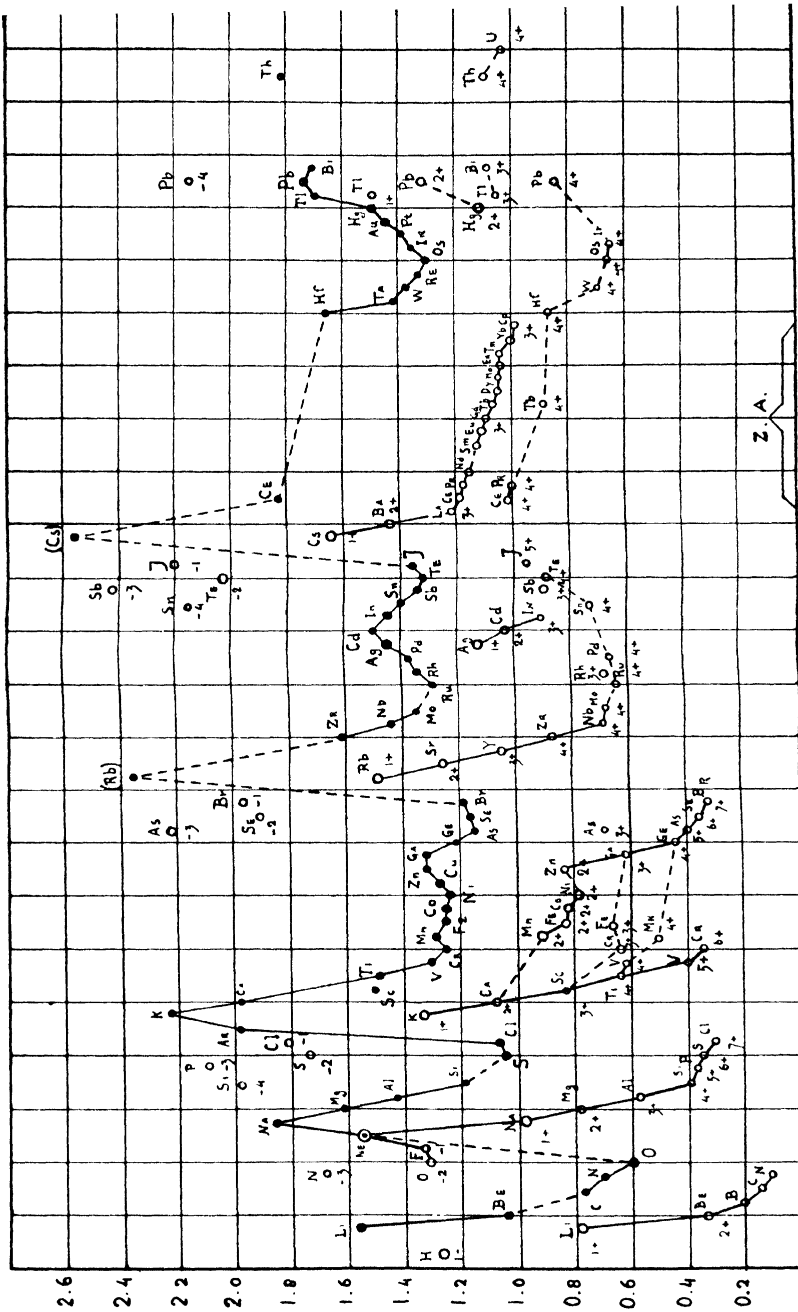

Fig. 3. Apparent Radii of Atoms and Ions in Crystals according to V. M. Goldschmidt.

apparent atom- and ion-radii according to GOLDSCHMIDT.[7]) If other circumstances are equally favourable, isomorphous substitution may be expected for particles lying close to a horizontal line; e.g.: Li — Mg, Na — Ca, Ca — Y; Mn — Fe — Co — Ni, Ru — Rh — Pd — Os — Ir — Pt, the rare earth metals mutually; Ag — Au, Hf — Zr, etc. etc. For the evident regularities in these combinations and their explanation I refer to the cited literature on geochemistry. By spectrographic methods a large number of elements illustrating these cases were detected in various minerals. Useful information on this subject is enumerated in a publication by A. A. FITCH.[8]) Later publications by GOLDSCHMIDT and his co-workers are to be found especially in the "Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen" (1930—1936).

If the analyst is guided by these considerations it is improbable that he will overlook important constituents. It is still better to test the material by spectroanalytical methods before starting a chemical analysis, but this will not always be possible. The spectrograph registers even traces of elements independent of the fact whether a certain element is suspected or wholely out of mind. Careful examination of the photograph reveals at once the presence of an element without special effort and without anticipation.

The presence of all the elements to be taken into account being known, the scheme for the analysis is to be devized. This is principally a problem of insight and "feeling" but also necessitates a knowledge of available procedures for the determination of the elements and all this will come only with experience. It is safe to plot the scheme in a diagram, as this gives a better general view and reveals possibilities and defects at once. The behaviour of the elements in the scheme under the various intended operations is to be considered and possible interferences are to be prevented. After some experience this part of the work will not cause unsurmountable difficulties, but it should always be done with painstaking care.

2. PREPARATION OF THE SAMPLE.

The value of an analysis depends almost as much upon the choice and preparation of the sample as on the carrying out of

the analytical operations. With regard to the choice it need only be remarked, that the sample should be representative of the whole mass whose properties are to be discussed from the results. For homogeneous substances just enough material to carry out the analysis, with the addition of a small surplus to be safe in case some operation has to be repeated, will be sufficient. Heterogeneous materials require more care in every respect. The mass to be taken is left to the judgment of the analyst; when necessary the material is reduced to smaller fragments and intimately mixed. By quartering or similar operations, the sometimes very large quantities are lessened until a convenient amount is reached. Oxidized or weathered parts are to be discarded or reserved for separate examination and should never be allowed to mix with fresh parts in one sample. The last treatment of the sample to make it fine enough for attack by fluxes or solvents depends on the nature of the substance and is consequently dealt with in the following chapters. Great care should be taken during this work to prevent contamination by foreign matter.

4. CALCULATION AND DISCUSSION OF THE RESULTS.

For this part of the work we discriminate between very accurate analyses or fundamental calculations, general analytical work and technical analyses. Table II *) gives for every element first the international atomic weight, in the next column the "atomic weights in air" rounded off to 0.01 % [9]), further the atomic weight rounded off to 0.1 %. [10])

The use of "atomic weights in air" prevents the necessity of applying a correction for buoyancy and was strongly advocated by SCHOORL. Except for particularly exact work atomic weights rounded off to 0.1 % will serve as well, and for a large number of technical analyses the application of the still more rounded off values is quite satisfactory. For convenience, a table of factors is added to the book (table III). **) All the data in tables II and III are based upon the latest procurable in Spring 1936,[11]). The calculations can be made with the aid of logarithms. For most analyses a slide-rule serves equally well, as indeed the

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*) p. 12—13. **) p. 237.

accuracy, attained with a 10 inch rule, is astonishing good. (The now cheap calculating-machines are very convenient and for stating analyses with a great number of constituents, registering listing-adding machines in combination with a stamp of the same interlinear space are valuable.

Discussion of the results is rather difficult from the chemical point of view exclusively. The requirement that the sum of the analysis ought to be very near to 100 % is necessary but not convincing evidence that the analysis is accurate. This subject is treated to some extent especially by HILLEBRAND and WASHINGTON. [12]) The average value of the sums of a large number of analyses was determined to be 100.12 %. This shows the tendency in complex analyses to yield slightly high results, due to small impurities in the reagents and attack of the apparatus besides a quantity of dust, which cannot be excluded even in very clean laboratories. So it will be understood that the allowable limit on the high side is somewhat greater, than that on the low one and that if in a series of similar analyses the sums are all low, this is strong evidence that some constituent has been overlooked. This speaks for placing the upper and lower limit at 100.50 and 99.75 % respectively. The allowable error is to be distributed equably over all the constituents. So the determination of an element which is present to some sixty percent should give values deviating not more than 0.25 % from the true value and consequently the extreme admissible difference in duplicate analyses will be 0.50 %. But owing to the fact that the absolute accuracy in gravimetric analysis is almost independent of the concentration, whilst the relative accuracy diminishes rapidly with the amount to be determined it is better, to allow for a larger error in the minor constituents at the expense of those present in large amounts. Finally in every case the permissible error for particular constituents and total sum is largely dependent on all the circumstances affecting the analysis and should be the subject of separate consideration.

As already stated, a satisfactory sum does not prove the analysis to be correct. In a defective analysis compensation of errors is possible, or a constituent may be weighed in the precipitate from another element, and in both these cases it is possible that the errors, though sometimes very bad, will not affect the sum. For example if titanium is not determined, it cannot be reported. whilst, according to the analytical procedure chosen, silicon and

iron or silicon and aluminium may give too high results. As titanium is present in a large number of substances in amounts from 0.5—5 %, on an average 1 % and its presence may be of considerable and disadvantageous influence on certain properties, non-determination of it is often a serious error.

Accordance of duplicate analyses also does not prove that the reported percentages represent the correct values, unless the methods whereby these results were obtained are entirely different. Otherwise a systematic error may be introduced that cannot be detected at all.

Generally all these faults are recognized easily by testing the various precipitates, obtained in the course of the analysis, quantitatively or qualitatively. The best remedy to avoid them, is repeated precipitations, this being a very effective way of cleaning precipitates from foreign substances.

The results are to be reported in a logical order of succession in exactly the amounts found in the analysis. Any recalculation, if necessary for comparison-purposes, should be stated in direct connection with the results originally found.

Sometimes other evidence will be of use in the discussion of the results. In analyses of minerals and rocks, a competent petrographer may give most valuable information on this subject. Quantitative determinations by micrometric measurements with such instruments as Integration-stages give the percentages by volume of a given aggregrate of minerals. [13]) Separation by heavy liquids will be mentioned under the heading mineral-analysis. All these and similar methods however are mere confirmations of results, otherwise obtained and by no means would they be able to replace chemical analyses. But it is possible that they may reveal at once obvious mistakes in the determination of some constituent and may afford (e.g. in the case of zirconia, phosphorus, rare earths etc.) more sensitive, rapid and convenient indications for the presence of an element than qualitative chemical analysis.

Table II.

ATOMIC WEIGHTS. [11)]

Symbol	Nr.	Element	International Atomic Weight	Atomic Weight in Air.	Atomic Weight rounded off	Symbol.
Ag	47	Silver	107.880	107.88	107.9	Ag
Al	13	Aluminium	26.97	26.96	26.96	Al
As	33	Arsenic	74.91	74.90	74.9	As
Au	79	Gold	197.2	197.2	197.2	Au
B	5	Boron	10.82	10.81	10.8	B
Ba	56	Barium	137.36	137.36	137.36	Ba
Be	4	Beryllium (Glucinum)	9.02	9.02	9.0	Be
Bi	83	Bismuth	209.00	209.01	209.0	Bi
Br	35	Bromine	79.916	79.90	79.9	Br
C	6	Carbon	12.00(5)	11.999	12.0	C
Ca	20	Calcium	40.08	40.07	40.1	Ca
Cb (Nb)	41	Columbium (Niobium)	92.909	92.90	92.9	Cb (Nb)
Cd	48	Cadmium	112.41	112.41	112.4	Cd
Ce	58	Cerium	140.13	140.13	140.1	Ce
Cl	17	Chlorine	35.457	35.444	35.44	Cl
Co	27	Cobalt	58.94	58.94	58.9	Co
Cr	24	Chromium	52.01	52.01	52.0	Cr
Cs	55	Cesium	132.91	132.85	132.85	Cs
Cu	29	Copper	63.57	63.57	63.6	Cu
F	9	Fluorine	19.000	18.99	19.0	F
Fe	26	Iron	55.84	55.84	55.84	Fe
Ga	31	Gallium	69.72	69.72	69.7	Ga
Ge	32	Germanium	72.60	72.59	72.6	Ge
H	1	Hydrogen	1.0078	1.001	1.0	H
Hf	72	Hafnium	178.6	178.6	178.6	Hf
Hg	80	Mercury	200.61	200.62	200.6	Hg
I	53	Iodine	126.92	126.90	126.9	I
In	49	Indium	114.76	114.76	114.7	In
Ir	77	Iridium	193.1	193.1	193.1	Ir
K	19	Potassium	39.096	39.08	39.1	K
La	57	Lanthanum	138.92	138.92	138.9	La
Li	3	Lithium	6.940	6.94	6.94	Li
Mg	12	Magnesium	24.32	24.32	24.3	Mg
Mn	25	Manganese	54.93	54.93	54.9	Mn

The atomic weights in air are valid for 760 mm Hg, when brass gram weights and smaller weights of nickel are used. As the atomic volumes are not additive for the alkalies and earth alkalies, their atomic weights in air have been computed from the values found for their compounds.

Table II.

ATOMIC WEIGHTS.[11]

Symbol	Nr.	Element	International Atomic Weight	Atomic Weight in Air.	Atomic Weight rounded off	Symbol.
Mo	42	Molybdenum	96.0	96.0	96.0	Mo
N	7	Nitrogen	14.008	14.00	14.0	N
Na	11	Sodium	22.997	22.99	23.0	Na
Nb	41	Niobium	92.91	92.90	92.9	Nb
(Cb)		(Columbium)				(Cb)
Ni	28	Nickel	58.69	58.69	58.7	Ni
NH_4	—	Ammonium	18.039	18.02	18.0	NH_4
O	8	Oxygen	16.0000	15.995	16.0	0
Os	76	Osmium	191.5	191.5	191.5	Os
P	15	Phosphorus	31.02	31.00	31.0	P
Pb	82	Lead	207.22	207.23	207.2	Pb
Pd	46	Palladium	106.7	106.7	106.7	Pd
Pt	78	Platinum	195.23	195.24	195.24	Pt
Rb	37	Rubidium	85.44	85.43	85.4	Rb
Re	75	Rhenium	186.31	186.32	186.3	Re
Rh	45	Rhodium	102.91	102.91	102.9	Rh
Ru	44	Ruthenium	101.7	101.7	101.7	Ru
S	16	Sulphur	32.06	32.05	32.05	S
Sb	51	Antimony	121.76	121.75	121.75	Sb
Sc	21	Scandium	45.10	45.09	45.1	Sc
Se	34	Selenium	78.96	78.95	78.95	Se
Si	14	Silicon	28.06	28.05	28.05	Si
Sn	50	Tin	118.70	118.70	118.7	Sn
Sr	38	Strontium	87.63	87.62	87.6	Sr
Ta	73	Tantalum	180.88	180.89	180.9	Ta
Te	52	Tellurium	127.61	127.6	127.6	Te
Th	90	Thorium	232.12	232.13	232.1	Th
Ti	22	Titanium	47.90	47.90	47.9	Ti
Ti	81	Thallium	204.39	204.40	204.4	Tl
U	92	Uranium	238.14	238.32	238.3	U
V	23	Vanadium	50.95	50.94	50.94	V
W	74	Tungsten	184.0	184.0	184.0	W
Y	39	Yttrium	88.92	88.91	88.9	Y
Zn	30	Zinc	65.38	65.38	65.4	Zn
Zr	40	Zirconium	91.22	91.22	91.2	Zr

For very accurate work, or for different conditions, (e.g. aluminium mg weights), it will be advisible to use the international atomic weights and to apply a correction for buoyancy. Generally, analytical errors exert much more influence on the result and rounded off values will be quite suitable.

OPERATIONS.

A few words may be devoted here to the scheme of training for the analyst. After a course of qualitative analysis it is most desirable that the chemist acquires a more thorough knowledge of the fundamentals of general and physical, — including colloid — chemistry. The border-line parts of mineralogy and general geology, including geochemistry as well as special parts of the biological (physiological) sciences, are, now more than ever, indispensable for arriving at a sound understanding of the inorganic processes in nature. Besides, a well trained hand, attentiveness, due deliberation and much experience should go hand in hand with theoretical knowledge. But when these conditions are fulfilled, quantitative analysis, far from being "the mechanical performance of such operations without understanding the reason for each step" will prove to be a prolific source of interesting scientific work, apart from the results which are often of the utmost importance for the advancement of chemistry and other sciences, commerce and industry.

A course of quantitative analytical chemistry should start with the learning of ordinary procedures and manipulations. In the Analytical Department of the Pharmaceutical Labaratory in Utrecht, Professor SCHOORL has introduced the following system: A number of well chosen preparations of pure chemicals are to be prepared by the student, starting from ordinary raw materials. These substances are consecutively analysed according to standard methods, whenever possible by two or more entirely different procedures. This scheme is applicable to gravimetric as well as to titrimetric methods with equal profit.

After these preliminary exercises the practice of quantitative analysis should be further learned in researches on the composition of actual samples. Rocks and minerals provide a large variety of samples of different complexity and are therefore very suitable for this purpose, as well as most of the other sub-

stances mentioned on p. 4. At first the student should work with portions of specially prepared mixtures of known composition. It is well to perform the analysis of the same sample more than once in different stages of the course, every time trying to obtain more satisfactory and complete results, whenever possible with quite different procedures. From the beginning, the student should make a liberal use of the laboratory library for consulting the literature in periodicals and preferably of a — though at first small — set of well chosen books of his own for quiet study of the principles. The course should be terminated by the analysis in duplicate of a number of different materials.

ANALYTICAL OPERATIONS.

After the preparation of the sample, the latter or separate portions of it are to be prepared for the carrying out of the analytical procedures. No general rules can be given for this part of the work and every case should be considered with the special purpose in view. Therefore, in the different chapters of this book, the particular methods of attack for the materials to be analysed will be given in full detail.

The *methods of gravimetry* can be divided as follows:

1. Residue determinations after heating or other special treatments of the sample.
2. Gas-evolution processes; the escaping gases are absorbed and weighed.
3. Precipitation processes and their converse: extraction processes.
4. Partition processes (liquation).

Besides, a few sensitive and specific colorimetric procedures, frequently used in rock- and mineral-analysis will be described.

1. Under the heading *residue determinations* can be ranged for example indirect determinations of water (water escaping below 105°), determination of loss on ignition (e.g. CO_2 in pure carbonates), ash determinations in organic materials, heating with fluxes or other reagents either wholly or partly volatile or nonvolatile (heating with solid ammonium carbonate of sulphates obtained by evaporation with sulphuric acid; treatment of the separated silica with HF and H_2SO_4 to determine the content

of impurities; thermal treatment of sulphates decomposable by heat in presence of zinc oxide in order to determine total water by retaining the acid with the added reagent), decomposition of carbonates with non-volatile acids with determination of loss in weight (Bunsen's method). All these reactions are ordinarily not very specific, but simple to carry out while the experimental errors in the procedure are often negligible.

2. Determinations of water and carbon dioxide for example, are to be classified under this heading.

3. Well-known procedures, the description of which forms a large part of the contents of this book, belong to this group. The precipitates can be ignited and weighed, dried and weighed, or other treatments, especially titrimetric procedures, may be applicable to them.

4. Though use is made of partition processes in inorganic analysis now and then, the principal applications will be found in organic chemistry.

In view of the importance of the third group, the uniform *practical* principles concerning the precipitation and further treatment of precipitates will be mentioned briefly here. It cannot be too strongly emphasized that every worker in analytical chemistry should make himself familiar with the theoretical fundamentals of even common analytical manipulations. Excellent books on this subject have been written [14]) and it is suggested that every chemist should consult these treatises at the latest when beginning the practice of quantitative analysis.

COMPOSITION OF PRECIPITATES.

It is preferable that the composition of precipitates remains constant under a wide range of experimental conditions holding at the time of formation but as this demand cannot always be satisfied, one often must have recourse to standard procedures under reproducible conditions. Neither of these alternatives is essential when, by suitable treatments, the precipitate can be changed into a form or compound of well-defined composition. Further it is desirable that precipitates or the form in which they are weighed contain only small percentages of the substance to be determined in order to make the results more accurate. Hence the general inclination to use organic reagents with

large reaction weights and yielding precipitates of definite composition. Following FEIGL, a very interesting suggestion for the determination of unweighable amounts of substances by multiplication of the precipitate may be given here for curiosity: after the formation of the still unweighable precipitate, the active component is regenerated and caused to react again, etc. while the inactive part accumulates steadily until a weighable amount is reached. The practical interest of this procedure, however, has not been demonstrated as yet; determination of potassium as chloroplatinate according to this suggestion may be possible, at least theoretically.

OTHER DESIDERATA FOR PRECIPITATES.

Whenever possible, the precipitation of an element should be selective and consequently not be hindered by other — especially related — elements. The precipitate should be very insoluble in the reaction-medium, easily collectable and readily washed free from contaminating matter, that is, it should not tenaciously include or adsorb other substances, nor form mixed-crystals with other compounds which are likely to occur in the final solutions.

SOLUBILITY OF PRECIPITATES.

A precipitate is formed ordinarily by exceeding the solubility-product of the compound. Consequently, this may be obtained by the addition of but one of the ions. In the case of an only slightly soluble precipitate, an absolutely small amount of one of the common ions already exerts a relatively considerable action with the result that the amount of the other ion present in solution may easily become negligible. This will be so during the precipitation where it is self-evident that an excess — however small — of the precipitant must necessarily be present, but during the washing of precipitates a common ion should be used in the liquid. If the added compound is not removed in the subsequent treatment of the precipitate, the final washings — when other impurities are absent — are made with the minimum amount of cold water. in the opposite case this precaution will not be necessary.

Some crystalline precipitates tend to form super-saturated solutions. This undesirable behaviour may be overcome by vigorous mechanical stirring of the solution and by allowing the liquid to stand for a long time. In a number of cases the solubility can also be decreased by the addition of alcohol to the solutions. A special case is formed by the precipitation by regulation of the hydrogen-ion concentration. Here there will often be an optimum concentration to be adhered to in the precipitation of a given element either on account of the amphoteric character of some hydroxides or by the possibility of exceeding the pH where other hydroxides also become insoluble. Precipitates having a tendency to pass through the filter in colloidal solution should be rinsed with an electrolyte solution to keep them in the flocculated form.

STATE OF THE PRECIPITATE.

Owing to their relatively high solubility some precipitates are obtained in a crystalline form, especially when formed in hot solution. Both working at high temperatures and ageing of the precipitate lead to formation of the more insoluble and easily filtrable coarsely crystalline precipitates. As the proportion mass to surface is also more favourable here, the adsorption of foreign matter is equally decreased.

Less soluble substances are obtained in a fine powdery form, these have a strong tendency to creep along the walls of beakers and funnels, consequently the filters should never be filled too high, especially in this case. If not impossible for other reasons, it will be best to precipitate these compounds at the boiling point.

Still finer precipitates (for example the silver halides) and still more, colloidal precipitates, require more care in every respect. But when prepared in the right way and especially when it is possible to mix some macerated filter paper with the precipitate the operations with these substances will not give unsurmountable difficulties.

COLLECTION OF PRECIPITATES.

This operation may be carried out by filtration or by application of the centrifuge, the latter instrument being extremely

useful when difficultly filterable precipitates are to be cleaned.

Formerly filtrations were made almost exclusively with cellulose, (viz. paper or cotton-wool) as material for the filter. This procedure is entirely satisfactory when the precipitates are to be ignited and on ignition do not change when in contact with burning organic matter. For other precipitates, perforated crucibles with asbestos or platinum-sponge layers have been in use since the end of the last century and have nowadays to some extent been resuscitated in the shape of various forms of filter-sticks. [15]) For both purposes, however, these materials as well as glass-wool have been largely displaced by porcelain, glass and fused silica.

As there are two contradictory desiderata for filters, viz. quickness of filtration and small pores, the required materials are all made with various diameters of pores to correspond to the particle-size as much as possible; most crystalline precipitates, however, can be prepared in such a form that the filtrate will run nearly almost as quickly as pure water through an ordinary filter. Rightly prepared, the colloidal precipitates are not so bad as is generally stated, and especially when thoroughly mixed with macerated filter paper these substances will filter very readily. In ordinary filtrations with paper, suction will not be necessary to increase the speed of filtration for most crystalline precipitates; with colloidal precipitates, suction is most objectionable as the pores quickly become clogged and channels are formed in the voluminous precipitate thus rendering thorough washing almost impossible. With filter crucibles as well as with colloidal filter-membranes of organic nature, suction is indispensable. [15a])

PAPER FILTERS.

The size of the paper should be chosen with regard to the mass of the precipitate rather than to the volume of liquid. For proper washing it is advisable, that the filter be filled to not more than one third, or at most one half, with the precipitate; for very small precipitates in a large bulk an intermediate course should be taken. The dry paper is folded in half and then again in half, so that a sector with angle 90° and four layers thickness is obtained. The folds are sharpened, but the top of the cone must

remain intact. The opened filter is placed in an analytical funnel with straight walls and an angle of exactly 60°, in which it will fit snugly after moistening the paper with water. To obtain a very rapid filtration, the filter should be "overfolded" slightly the second time, and then opened on the larger side. Thus prepared, the filter will touch the funnel only about half of the cone, the lower part being free from the glass (fig. 4a).

Analytical funnels should preferably be made of some resistance glass, have straight walls, a top angle of very nearly 60° and a stem with an internal diameter of from 3—5 mm and 10—15 cm length. Analytical funnels of Jena glass are now available with angle of exactly 60° and with channels for rapid filtration, so that the filter need not be overfolded. (fig. 4b) After the paper has been put in place, the filter is filled with water, any air bubbles are carefully removed, by gently pressing the paper to the walls especially those which remain tenaciously along the folds. Water will now pass readily through the filter and it will not be difficult to fill the stem. The column of water under the filter exerts a very profitable suction, but this must not be exaggerated by fitting funnels with stems of 30 cm and more. It is not necessary to cut off the stem straight but this will aid in keeping it filled with water.

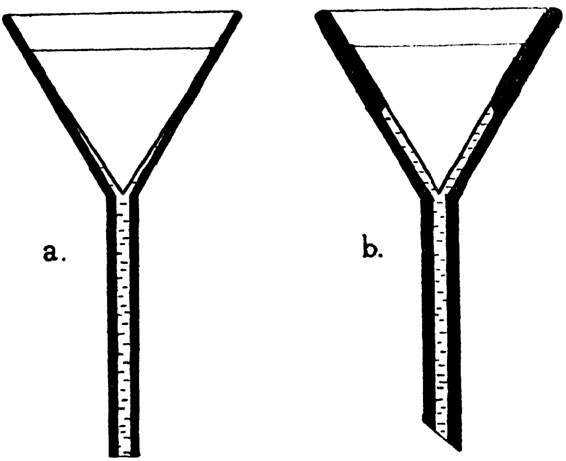

Fig. 4.

The glass wall of the funnel should project about 1.5 cm over the rim of the paper. This part of the funnel should never be allowed to become wet, otherwise loss of the precipitate by creeping etc. may occur. The opening of the stem of the funnel should be at a height of 2—3 cm above the surface of the liquid. The stem should be as near to the wall of the beaker as possible without touching it, to avoid splashing by the falling drops.

The use of *filter paper pulp* in filtrations of colloidal precipitates is a decided improvement. [16]) Furthermore the precipitate remains in a finely divided state after ignition and this is very welcome if further treatment of the precipitate is intended, particularly in the determination of iron, as any magnetic oxide which may have formed is easily re-oxidized. The pulp should be added after the final formation of the precipitate as some precipitates tend to make the fibres fireproof and also, as, the action of acids on the organic matter may form compounds that interfere with some precipitations, viz. of aluminium as hydroxide.

In filtrations under suction, the action of the pump should be applied gradually and gently and a platinum cone of 60° of diameter 2.5—3 cm, perforated with many small openings will be required to support the top of the paper. It is desirable to have a large volume of air between the pump and the filter apparatus to lessen accidental variations in pressure and to avoid back flow of water from the pump. The necessary apparatus will be described in the section on filter crucibles. For preparative work, BÜCHNER-funnels of porcelain or preferably of Jena glass are indispensable for supporting the flat filter paper.

Filter crucibles are extremely valuable apparatus when used in the right way; they unite the properties of filter, funnel and crucible in one piece and are available in different pore-sizes, the smallest retaining even the finest precipitates. A filter tube should be fitted to the crucible with a piece of soft rubber tubing; a piece of 5—6 cm length of bicycle inner tube will serve for the purpose. The use of an Erlemeyer suction flask is an objectionable practice unless the filtrate is not required. Therefore, WITT's filtering apparatus or a simple bell-jar on a ground glass plate should be used in filtrations with suction. The filtering tube may be straight when an erlemeyer is used to catch the filtrate; when a beaker is used a bent tube will be necessary to prevent splashing of drops. A three-way cock is required to apply or stop the suction in a convenient way (fig. 5 a and b). As filter crucibles with layers of sintered glass, porcelain and fused silica are entirely satisfactory, the description of the preparation of an asbestos layer in GOOCH crucibles and of a platinum sponge mat in MUNROE (NEUBAUER) crucibles is omitted here. [17]) Glass filter crucibles should not be heated to more than 250°, porcelain crucibles stand careful heating at temperatures

of more than 1200°, provided a crucible cap is used, otherwise the bottom will crack.

CLEANING OF PRECIPITATES.

Three general rules for the washing of precipitates should be kept in mind:

1. The total volume of wash-liquid should be kept as small as is compatible with thorough washing, 2. It is much better to

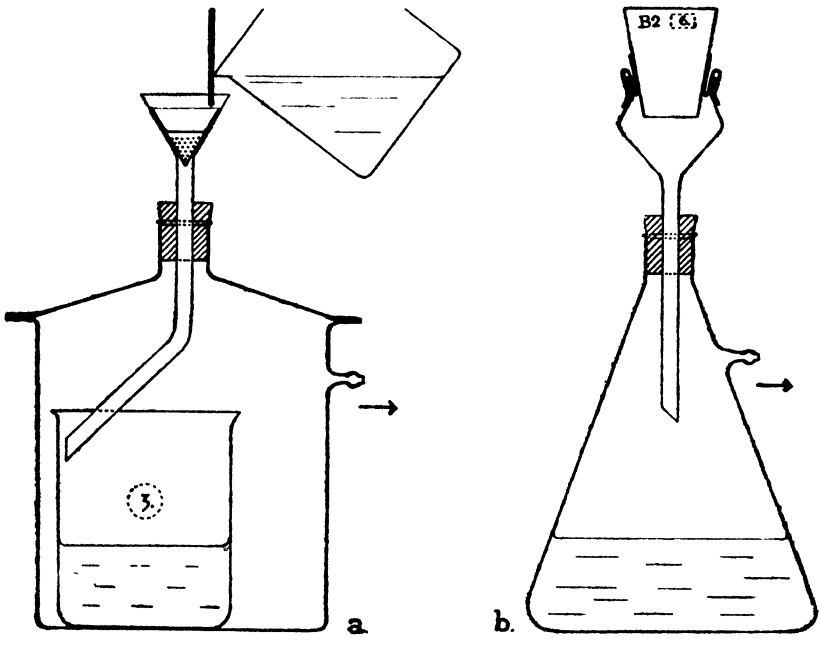

Fig. 5a. Witt's filtering Apparatus with Funnel, Platinum Cone and Filter.
Fig. 5b. Filtration Flask with Filter Tube, Rubber Connection and Porcelain B_2 filter Crucible.

wash with a larger number of small portions — the filter being allowed to drain completely after each addition of wash-liquid — than with a small number of large portions, 3. A common ion should be employed in the wash water whenever possible.

Precipitates which are liable to oxidation etc. on being exposed to the air e.g. many sulphides, should remain covered with the

liquid during the washing process; ordinarily the washing of these precipitates will require much more liquid and time. The section on the solubility of precipitates is of direct interest also for the washing of precipitates (p. 17). Care should be exercised in properly washing the upper parts of the filter and avoiding the precipitate creeping over the rim.

The best method, however, to obtain precipitates of the desired composition and at the same time free from contaminating matter is by repeated precipitation of the dissolved precipitate. This procedure is still more to be recommended, especially in accurate work, as it demands only a fraction of the time, necessary for complete washing and is less tedious to carry out. The necessary number of washings and re-precipitations must be considered after each precipitation; ordinarily 4—6 washings combined with double precipitations are quite sufficient, but in some cases these numbers have to be increased.

TREATMENT OF PRECIPITATES.

Consequently the whole treatment of precipitates will be as follows:

When the precipitate has settled somewhat, the completeness of precipitation is secured by the further addition of a few drops of the precipitant. After standing in the covered beaker during the allotted time after precipitation, — when desirable at first in a warm place, later in a cool one — the apparently clear supernatant liquid is decanted from the precipitate and the latter washed by decantation *in the beaker*. The whole amount of liquid should be filtered through the paper, the stream of fluid being directed by a thin stirring-rod. If necessary, the beaker is placed in an inclined position when liquid is not being added to the filter to prevent disturbing the precipitate. Finally the precipitate is brought on the filter by means of a stream of the wash-liquid, the beaker with stirring-rod being manipulated by the left (right), the wash-bottle by the right (left) hand; when necessary, a stirring-rod with a one piece pure rubber cleanser may be used in this operation. Washing of filter and precipitate is continued until considered complete; usually this may be tested by catching a few drops of the filtrate in a test tube and testing for a definite constituent or by evaporating a

few drops of the filtrate on a piece of platinum foil or the lid of a platinum crucible. When a re-precipitation is intended the filter is carefully loosened from the funnel at one side to empty the stem after which funnel with filter and precipitate are taken out of the funnel stand, held in a nearly horizontal position over the beaker used in the precipitation and the precipitate is washed back into the beaker by a stream of clean water. The filter is thoroughly washed in the funnel and may conveniently be used in the subsequent filtrations. Before a re-precipitation or if only the filtrate is of interest, the precipitate need not be quantitatively transferred to the filter.

DRYING OR IGNITION OF PRECIPITATES BEFORE WEIGHING.

Precipitates to be weighed after drying at low temperatures, or those, changing their composition when in contact with burning paper, should be caught in a filter crucible. The crucible with contents is dried at the requisite temperature in an oven provided with a thermometer; in case of an ignition the temperature should be raised very gradually to avoid losses by decrepitation. Electric ovens with a temperature control are very convenient for this purpose. Precipitates on filter papers are transferred moist to the crucible and wrapped up in the paper to prevent mechanical losses. The crucible is placed in an inclined position on a triangle at about 6 cm over the *very low flame* of a Bunsen burner, protected against draught by a flame-screen. Very gradually the height of the flame is increased. This will cause the charring of the paper and this must be carried out *at as low a temperature as possible* to prevent ignition of the paper (this will inevitably cause mechanical losses of the precipitate) and also because the carbon obtained at a low temperature is burnt off much more easily than carbon resulting from rapid heating at high temperatures. When vapours are no longer liberated, the height of the flame is again increased, so that the bottom of the still inclined crucible becomes dull red. This state is continued until all of the carbon is incinerated, after which the heating may be commenced at the temperature required to bring the precipitate into a definite condition. Here only, the lid of the crucible may be necessary to increase the temperature. The flame should not be allowed to envelope the

whole crucible as a reducing atmosphere around the precipitate would be the result; in some cases the flame gases should even be kept away from the contents by a protecting asbestos or platinum screen with a hole to fit the crucible. Ordinarily a blast is not required, but if so, the flame should embrace only the lower two third parts of the vertical crucible and consequently not be directed vertically on the bottom. Tripods are quite unsatisfactory in ignitions as their height cannot be adjusted properly. Ring stands with heavy bases are the only appropriate apparatus of this kind in analytical laboratories.

After ignition, the covered crucible is allowed to cool completely to room temperature, preferably in a dessicator with a powerful dessicant. Platinum crucibles cool very quickly, provided the space in the dessicator is not too small. On the contrary, in large dessicators it is almost impossible to maintain the required atmosphere when these are frequently opened. A re-ignition should be made, until two subsequent weighings yield the same result. It is advisable in this case to prepare the weights on the balance beforehand in a second or further weighing to prevent the adsorption of moisture from the air as much as possible.

WEIGHING.

The weight of a precipitate is obtained as the difference of the weight of the crucible with precipitate and the weight of the crucible alone. It is necessary that the apparatus — the weight of which should not be affected in the analytical procedure — be treated in the same way when weighed alone as with the precipitate. Consequently, when a precipitate is to be ignited at 1000°, when determining the weight of the crucible this should be heated also to 1000°. Sometimes the weight of the crucible may change slightly in prolonged ignitions. In this case the weight should be determined directly after removing the precipitate with such reagents as will not affect the weight of the crucible. Only glass or metal apparatus should be placed directly on the pan. These objects should be perfectly dry and clean and should have the same temperature as the balance, otherwise the thermal equilibrium in the balance will be disturbed and consequently the weighings inaccurate during the

time required for the re-establishment of uniform temperature. The weights should always be placed on the right hand pan and a set of weights should be calibrated every now and then in accurate work. It is not necessary that the weights of the set are absolutely correct, but the various weights should have the right proportions of mass and they should be used with measuring apparatus with consistent volumes. Therefore all these apparatus in one laboratory must be adjusted in the same way. [18])

Weights and objects to be weighed should be handled exclusively with ivory-tipped forceps and platinum-tipped or other tongs. Records should be made in a uniform manner in a notebook reserved for this purpose. The procedure of weighing is extremely simple, if carried out systematically. The arrangement of the weights will be seen in fig. 6; the heaviest weight is placed in the centre of the pan, the other large weights are arranged in a symmetrical manner around it, to avoid swinging of the pan on releasing. The weights below the gram are placed alongside each other in two rows, thus facilitating the reading. It is, however, in the end a saving of time and indeed of money too, to use balances requiring only the gram-weights to be placed on the pan. The approximate weight of the object is determined on a letter-balance and the required larger weights placed on the pan. With a system of levers the other weights in the form of riders are released and placed subsequently on the balance beam. With this type of balance the milligrams and tenths are ordinarily read directly on a scale.

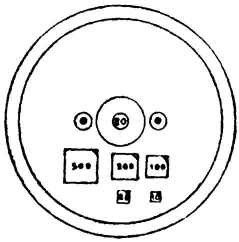

Fig. 6.

Portions for the decomposition are weighed out by the *method of addition;* the crucible or other apparatus that will serve in the subsequent operations is weighed empty. The sum of the weights on the right pan is increased to somewhat below the total of weight of the crucible with the desired amount of sample or flux. Next the cover of the crucible is placed in the centre of the left pan and the crucible is placed in front of the balance. About the required amount is transferred by the aid of a small spatula (to be reserved for this purpose in the balance case) from the sample tube into the crucible, the latter is replaced on the lid and by cautiously releasing the pans, the necessity of

further addition or of pouring out a little from the powder is ascertained. The powder should not be allowed to form a deposit on the upper side of the walls of the crucible.

Hygroscopic powders are weighed *by subtraction;* viz. a specimen tube, containing the compound in question is weighed, then quickly but cautiously, about the amount required is poured out into a suitable receiver and the closed specimen tube is re-weighed. The difference represents the exact weight of the portion.

When the accurate weight of an amount of substance need not be known, it is preferable to provide both balance pans with a filter paper of equal size. These are ordinarily similar in weight within a few milligrams and this difference will generally be of no consequence in the case of weighing fluxes or when solutions for washing etc. are to be made up.

COLORIMETRIC COMPARISON. GENERAL REMARKS.

For a number of elements occurring in rocks and in most minerals only in minute amounts, gravimetric procedures are liable to yield erroneous results. For some of these elements, accurate colorimetric procedures have been worked out. Though the relative accuracy of colorimetric procedures is not very great — errors of 5—10 % may be expected on an average — the absolute accuracy for small percentages is ordinarily far superior to that of gravimetric and often also of titrimetric methods.

In colorimetric work it is generally assumed, that the intensity of the colour in a given solution is proportional to the amount of the coloured compound. On this supposition — viz. that the law of LAMBERT-BEER is valid — are based the well-known colorimeters of DUBOSQ, STEIGER, SCHREINER and others where the length of the light path in the solution is variable and may be read on a scale. These instruments, besides being very expensive, have the drawback that they are not universally applicable. Therefore, in general and for the analysis of minerals and rocks in particular, the simpler procedures and instruments are better. These methods are based on the fact, that when *under the same circumstances* the same colour is obtained in test-solution and standard-solution by appropriate dilution these liquids have the same concentration of the compound to be determined. The

colours may be compared: 1. with a colour scale, 2. in a colorimeter fitted with two cells of the same dimensions, by simple dilution of the strongest solution with water, 3. by the procedure of titrimetric colorimetry.

DESCRIPTION OF COLORIMETRIC PROCEDURES.

1. A colour scale is most useful when a large number of determinations are to be made within the short life of the standard colour scale.

A number of test tubes of about the same diameter are selected by filling the dry tubes — by means of a pipette — with equal volumes of water and discarding those in which the length of the column deviates more than 5 % from the average. Standard solutions are made of increasing concentration and filled to the same height in the tubes in a stand. The test-solution is treated in the same way and its place in the row is determined by visual comparison.

2. A colorimeter of this type is described by HILLEBRAND as "first Survey form" (UNITED STATES GEOLOGICAL SURVEY) and consists of two glass cells each with two plane parallel surfaces, at the same distance from each other in both cells. The other sides are blackened externally and to exclude further the effect of side light, the cells are placed in a simple, light box, stained black inside, one end closed by a piece of ground glass, the other being open. Provision is made that all light can be cut off, except that which comes through the liquid. Any suitable amount of the standard solution, which is purposely made stronger than the solution to be tested, is placed in one of the glasses and an indefinite part or the whole of the test solution in the other. Water is then added from a burette to the standard until there is no distinction as to colour. Perfect mixture is brought about by a glass rod flattened at one end. In making the colour comparison the box is best held close to a window, so as to get a full, strong light. Daylight is far preferable to artificial light. The amounts of the substance to be determined and that in the standard cylinder are of course proportional to the volumes of the solutions. [19])

3. The method of titrimetric colorimetry has been the subject of study by WINKLER and recently especially SCHOORL and

KARSTEN.[20]) The limits of the method have been enumerated by the latter authors:

a. The reaction should be simple to carry out, without special manipulations e.g. heating, partition processes etc.
b. The speed of the reaction should be large enough here as well as in direct titrimetric procedures.
c. The reaction-product should be rather stable.
d. The order of succesion of the addition of the reagents should be without consequence.

The procedure of titrimetric colorimetry is described by KARSTEN as follows: The test solution is transferred to a Nessler tube, the required reagents are added and the liquid is made up to a definite volume, either 50 or 100 ml. To another Nessler tube of exactly the same diameter add the *same* amounts of reagents and dilute with water until near to the mark. A standard solution of the compound to be determined is dropped from a burette into the cylinder until after vigorous stirring with a rod, flattened at the end, the intensity of the colour is the same in both tubes; by the addition of a small amount of water both volumes should be made exactly alike.

Cylindrical tubes of dark paper are slipped over the Nessler tubes before the comparison, to exclude side light. The tubes are placed on a thin plate of colourless glass over a turnable piece of white cardboard to yield a suitable diffuse light. The reverse side of this cardboard should be blackened to make the instrument applicable for nephelometric comparisons. A special outflow tube for the burette with a horizontal part about 5 cm long is described by KARSTEN; this serves to avoid interference with the observation of the colour.

In this institute, ordinary paint has proved to be a suitable cement for the glass cells. The objects should be allowed to dry thoroughly under pressure. Cells with fused connections (SCHOTT & GEN. JENA) are, however, far preferable.

LABORATORY AND LABORATORY WORK.

A few suggestions may be made for the independent worker as to the equipment of the laboratory, though in most cases the locality will exist already and radical changes will neither be required nor possible. A list of apparatus mentioned in this book

has been added p. 242, and these will be at hand or can be built up in any well equipped laboratory. For a number of the more complicated apparatus, it is a saving of time to make them permanent and ready for direct use as is the uniform practice already with apparatus for organic analysis with combustion methods. For efficient work the analyst should dispose of ample room — a work-bench of 6 m or more will be required — and of a complete outfit for analytical work. This, however, holds chiefly for a very experienced worker, able to supervise a number of simultaneous operations. In a hood with a good draught, the water-baths and two stands for evaporations in a hot air-bath or over the free flame are placed; a separate small hood for evaporations with hydrofluoric acid will be welcome. Provision should be made to keep the whole laboratory as clean as possible and the air free from fumes and dust. The almost uniform practice of placing the bottles with reagents in a stand in front of the analyst on the work-bench cannot be too strongly deprecated as it is a continous source of contamination of — necessarily — uncovered vessels and a possibility of breaking or disturbing apparatus; the same may be said of cocks and connections for gas, water, air and electricity; these should be in front of the work-bench instead of at the back, unless there is much free space to attend to them. The author has found it to be most convenient to place the bottles with reagents together with beakers wherein a precipitate is allowed to form and settle during any considerable time, on a long, narrow table behind the operator. Reagent bottles with concentrated acids are placed on a glass plate. Convenient caps for otherwise unprotected flasks, especially those with cork stoppers, are small beakers, preferably old scratched specimens, unsuitable to serve further in precipitations.

Vessels standing for any length of time should be effectively protected against dust even when evaporations are carried out in them, either by clock-glasses of suitable dimensions or screens of glass, wood or cardboard.

The quality of the reagents used, is of the utmost importance in careful work as large quantities of reagents are employed during the performance of the analysis. The reagents should be tested for impurities; for example the author has never succeeded in obtaining calcium carbonate for the determination of alkalies in silicates of sufficient purity, except when specially prepared

in the laboratory. Water, hydrochloric acid and especially ammonia water should always be prepared at short intervals by distillation as relatively enormous quantities are used in most analyses. Most other reagents can be obtained of satisfactory quality from dealers in chemicals; these should be purchased in not too small quantities to avoid waste of time in testing their amount of impurities. A list of reagents has been likewise added to the book (p. 250).

In carrying out *blank-determinations* it will not always be sufficient to perform the operations with the reagents alone as other errors may be introduced by the changes of conditions due to the much larger quantities of precipitates in actual analyses. Sometimes this difficulty can be overcome by taking a known amount of a very pure substance for the "blank-determination", in other cases, however, this will not be possible.

Solutions of solid reagents should as a rule not be made up and stored in glass bottles as many of them attack glass considerably. The required amount should be dissolved in the appropriate quantity of solvent when needed.

The balance should be in a separate room to protect it against acid fumes and dust from the laboratory. In the same room are conveniently placed other indispensable apparatus of the same delicacy e.g. microscope and other optical apparatus.

As advocated by WASHINGTON, it is advisable not to wear an apron in an analytical laboratory, except when cleaning apparatus etc., as this practice may lead to careless and slovenly habits: "If the analyst is liable to drop acids on his clothes he is more than liable to spill some of the solutions he is analyzing".

METHODS OF ANALYSIS.

ANALYSIS OF SILICATES.

Under this heading the analysis of the following substances: Silicate rocks, minerals, soils, sandstones, clays, laterites, bauxites, cements, slags, coal-ash (plant-ash) and glassware will be dealt with.

Silicate Rocks. General Considerations.

In the case of igneous *rocks,* qualitative analysis will be seldom required, as the main constituents are always the same, their amount is almost never negligible and so these elements must be determined in every case. The general type of composition then affords indications as to the minor constituents that will occur and from this point of view it is convenient to distinguish between three different types of rocks. Representative analyses for these types will be found in table IV, together with the range of variation for silicate rocks.

Table IV.[21])

Type	I	II	III	
SiO_2	48.23	60.44	51.93	30—80 %
Al_2O_3	18.26	16.65	20.29	0—25
Fe_2O_3	1.26	2.31	3.59	0—13
FeO	6.10	3.09	1.20	0—15
MnO	n.d.	0.13	n.d.	0—0.5
MgO	10.84	2.18	0.22	0—30
CaO	9.39	4.22	1.65	0—17
Na_2O	1.34	5.18	8.49	0—14
K_2O	0.73	2.71	9.81	0—12
H_2O+	2.00	1.07	0.99	0—12
H_2O-	0.26	0.36	0.10	
TiO_2	1.00	0.60	0.20	0—5
CO_2	0.43	0.48	0.25	0
P_2O_5	0.07	0.29	0.06	0—1
rest	—	0.25	1.80	
Sum	99.91	99.96	100.58	—

I Bronzite norite, Crystal Falls, Michigan. Analyst: G. Steiger.

II Diorite porphyry, La Plata Mountains, Colorado. Analyst: W. F. Hillebrand.

III Pseudoleucite-sodalite tinguaite, Bearpaw Mountains, Montana. Analyst: H. N. Stokes.

Between types I and II all possible transitions and even more extreme species are possible which range from ca. 35—80 % total silica. In the more "basic" types magnesia predominates over all other bases, but iron never fails to be present. They merge gradually into rocks like no. I where iron, magnesia and calcium are more or less equivalent and alkalies are present to some few percent. Aluminium accompanies these elements in the dark minerals as well as in the colourless species, the maximum percentage occurring in the intermediate rocks. The oxides forming dark minerals (magnesium, iron and calcium) become less important as silica increases. The type represented by analysis no. II is composed mainly of light minerals, the alkalies become more and more important and an excess of free silica may be present in the form of quartz or tridymite. The end of magmatic differentiation is probably represented by the eutectic composition of quartz and feldspars with 75—80 % total silica, (VOGT). There is still another series of rocks, the main difference between this and the former being that the alkalies play a much more important role in their composition. A typical "alkali-rock" is given in analysis III, table IV. Owing to this large alkali-content there is never free silica in true representatives of this group, as the alkalies require six mol SiO_2 to 1 mol $(Na,K)_2O$ to be wholly "saturated". The genetic position of the alkali-rocks is, as yet, an unsolved problem. Aluminium oxide is present in such large amounts as to crystallize sometimes as such in the form of corundum. The "femic"-oxides may vary in amount, but generally calcium and notably magnesium diminish more than iron. Together with these properties there is another peculiarity: a large number of rare elements is concentrated in the alkali-rocks and this induces the formation of minerals built up more or less substantially from these elements, thus giving rise to the considerable remainder in analysis III. Among these elements are found; Li, Be, B, C, F, P, S, Cl, Sc, Rb, Y, Zr, Nb, Mo, Sn, Cs, Rare earths, Hf, Ta, W, Th, U, and sometimes in amounts that warrant their determination.

In other rock-types the variety in minor constituents which can be detected chemically is less pronounced. The basic "alkali-calcic" rocks contain remarkable quantities of metals of the iron-group together with Ti, V, Cr, whilst all occurences of platinum metals are also associated with them. Acid rocks of this type contain larger amounts especially of B, F, Cl, Sn, W

and seem to merge rather gradually, in this respect, into alkaline rocks. In general, rare elements play only an unimportant role in intermediate rocks from the alkali-calcic type. These geochemical considerations, together with petrographical evidence, give indications to the analyst as to the constituents which should be looked for.

PREPARATION OF THE SAMPLE.

Enough of the rock to give a representative sample is crushed with the aid of a "geological" hammer (hardened steel) on a steel plate. The rock is placed in a small bottomless box to prevent fragments flying. The fragments are one by one crushed in a steel "diamond" mortar preferably by one heavy stroke on the pestle and without any rotary motion of the pestle in the mortar as this inevitably causes abrasion by mineral fragments between pestle and cylinder. After the whole material has undergone this treatment it is sifted; with the remaining large fragments the operation is to be repeated until all will pass readily a sieve with openings from 1.5 mm in diameter. This powder is crushed in an agate mortar and sifted until no fragments larger than 0.3 mm are present. This will be fine enough for most determinations. Contamination by the material from mortar and pestle is very slight. On carefully crushing 20 g of quartz, 0.0163 g iron oxide could be detected. This gives an error in the determination of 0.08 % plus for iron and in most cases this does not matter. Quartz has a hardness 7 in MOHS' scale. With albite (hardness 6) the amount of iron becomes almost negligible (0.014 %). The abrasion of the agate mortar can be neglected altogether, as the amount of silica present in the rock is only slightly influenced by it. In special cases one should be certain that neither the mortars nor sieves contain elements that are to be determined and are only present in *small amounts* in the rock. Care should be taken that the whole amount is passed through the various operations as otherwise the tougher minerals would not be present in their due percentage in the sample.

Too fine grinding is unnecessary for the decomposition and is even harmful, as oxidation of ferrous iron is promoted and the amount of hygroscopic water increased by it, whilst variations

in the water content of the sample, due to fluctuations in the relative degree of moisture in the air, become troublesome.

Finally the powder is thoroughly mixed and after lying a few hours in the air, protected against dust, to make sure that it is in equilibrium with the water-content in the laboratory-atmosphere, it is stored in a tightly closed sample-bottle. The analyses should not be carried out with specially dried powder as this inevitably takes moisture from the air. If all the portions needed for the analysis are weighed succesively or on the same day, the moisture need be determined only in one of the portions, otherwise every portion weighed out under different conditions should be dried at 110° and weighed again directly after room-temperature is reached but this is not recommended.

STATEMENT OF ROCK ANALYSES. [22])

The final statement of the analysis should give at least the following constituents as they are always present in amounts that are easily detected in portions of from 0.5—2 g: SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, H_2O +, H_2O —, TiO_2, CO_2 and P_2O_5. Whether other elements are to be taken into account, depends on the nature of the material and the completeness claimed for the analysis. The order of statement may be justified as follows:

The acidic element which largely determines the character of the rock is reported first of all. The other elements are given in the order which brings together the natural groups, obvious in mineralogical associations, course of analysis and increasing electropositive character. Water and carbon dioxide are reported together as these determine the degree of weathering of the rock. Distinction is to be made between water escaping at a temperature near 100° and the rest of it, the latter representing largely constitutional water, whilst water below 100° is mostly merely hygroscopic and in most cases unessential for the composition of the rock. The place of TiO_2 is more or less uncertain; [23]) consequently it is given separately, and finally phosphorus pentoxide is given, as it is present ordinarily in the form of a particular phosphorus-mineral; apatite. Silicate analyses should always be reported in this same order, the general composition of the rock can then be seen at first sight.

The arrangement of the minor constituents is not of great importance and may be guided by the same considerations which were developed for the major elements, but depends also on the object with which the examination for them was made.

GENERAL COURSE OF SILICATE ROCK ANALYSIS.

In rock analysis enough material is ordinarily available to dispense with the necessity of economising with the sample and therefore a number of separate portions will be examined if this is convenient or will make the determinations more accurate.

The constituents of rocks which may be advantageously determined together in *one* portion of the sample are indicated in the following scheme in vertical columns. The approximate amount to be reserved for every portion is also indicated.

1	2	3	4	5	6	7	8	9, etc.
SiO_2 Al_2O_3 Fe_2O_3 TiO_2 (ZrO_2) CaO MgO (SrO) (P_2O_5)	Na_2O K_2O (Li_2O) $((SiO_2))$ $((Fe_2O_3))$	FeO	$H_2O +$	$H_2O -$ MnO (P_2O_5)	(P_2O_5)	CO_2	S BaO Cr_2O_3 ZrO_2 R. E.	p. m.
0.5—1.0	0.4—0.6	0.5—1.0	0.5—1.0	1—2	1.0	1—5	1—2	p. m.

(( )): control-determinations.
( ): optional determinations.
R. E.: Rare Earths.

1. The *main portion* is fused with sodium carbonate to decompose the insoluble silicates and the cake is dissolved in hydrochloric acid. The solution is evaporated and after thorough dehydration, the silica will be insoluble and is filtered off. The silicic acid always carries down some impurities, for which a correction should be applied; so, after ignition, the silica is evaporated with the aid of hydrofluoric acid, the impurities are weighed and added to the filtrate from the silica. In this liquid the next operation will be precipitation of a number of elements

in the form of their hydroxides by just neutralising the solution, with ammonia. Under conditions securing the exact regulation of pH within narrow limits to 7, in the absence of carbon dioxide and with double precipitations, this affords almost complete separation of iron, aluminium, chromium, rare earths, titanium, zirconium and phosphorus (all of these going into the precipitate), from alkaline earths, magnesium, *manganese* and alkalies (remaining in solution). In the filtrate, calcium and strontium are precipitated as oxalate and magnesium either with a soluble phosphate as magnesium ammonium phosphate or with 8-hydroxyquinoline.

The ammonia precipitate can be treated in several ways. The combined hydroxides may be ignited and the elements weighed as oxides. It is, however, difficult to get alumina entirely free from water and not hygroscopic without simultaneous reduction of part of the iron leading to formation of Fe_3O_4, magnetite and consequently to low results. So, I believe it best, to separate this complex mixture direct after precipitation with the aid of sodium hydroxide solution. Aluminium, phosphorus and the like form soluble compounds, whilst iron, chromium, rare earths, titanium and zirconium remain undissolved. This remedies also another defect; in most analytical procedures alumina is determined by difference and accordingly, all the errors in the other elements of this group re-appear and accumulate in the figure for alumina. On the contrary, by applying the sodium hydroxide separation, aluminium can be determined conveniently in the filtrate, a correction being needed only for phosphorus. The reagent is now obtainable of highly pure quality (from sodium; e natrio) and if properly carried out, this method proves to be very satisfactory and convenient, whilst excessive contamination by attack from the glassware need not be feared and can be entirely prevented by working in small platinum apparatus. The description of alternative methods, however, will not be omitted.

2. In the early days of quantitative analysis the alkalies were reported exclusively by difference. The BERZELIUS method (attack with hydrofluoric acid, followed by precipitation of all the other elements) was a decided improvement, but formerly the separation of magnesium from the alkalies was tedious and inelegant (the newer organic reagents prove quite satisfactory here) and the separation of the alkali metals required much skill and patience.

The simplest method for the determination of the alkalies was worked out by J. LAWRENCE SMITH and is presented in this book with slight modifications by the author. The silicate is decomposed by igniting the fine powder with an excess of calcium oxide and chloride. Both of these have dual purposes, the lime besides being a strong decomposing agent, prevents the mass from fusing together, while the calcium chloride acts as intermediary by dissolving some lime, bringing this in intimate contact with the rock powder and at the same time providing the necessary amount of chlorine ion, to unite with the alkalies. Afterwards, the lime serves also as precipitant in the subsequent leaching of the cake. After separation of the lime with ammonium carbonate, a solution is obtained, containing only alkali chlorides together with ammonium salts. The latter are expelled by gentle heating, the alkalies weighed as chlorides and separated in one of the usual ways.

3. Exact gravimetric procedures for determining the amount of iron present in the bivalent condition are unknown. Hence this constituent is found by titrating an acid solution with some oxidising agent of known strength, ordinarily potassium permanganate or dichromate. Decomposition is effected by solution of the powder in a mixture of sulphuric and hydrofluoric acids; sometimes sulphuric acid alone will serve. When other oxidisable matter is present, corrections should be applied and in some cases, notably when organic matter interferes, correct values cannot be secured at all, as neither a definite end-point is reached nor can oxidation be expected to a definite level.

4. Total water can be found in a limited number of cases as loss in weight by heating the rock powder either alone or with a flux like borax. This presumes the absence of other volatile substances e.g. carbon dioxide and of constituents which change in weight on ignition e.g. ferrous iron etc.. Of universal application are the methods where the amount of water, which is liberated by heating either with or without fluxes, is caught in absorption tubes or by cooling (PENFIELD method etc.), precautions being taken to prevent reduction of the water vapour to hydrogen and also of simultaneous absorption of interfering substances e.g. chlorine or sulphur oxides.

5. Water escaping near 105° or 110° is estimated by drying a somewhat larger portion of the rock in an oven at these temperatures. The same portion can be advantageously taken for the

determination of phosphorus and manganese or the latter alone if phosphorus was separated in the main portion. Therefore the powder is decomposed with hydrofluoric and nitric acids, and aliquot volumes of the solution taken for the analyses. Phosphorus is precipitated as ammonium phospho-molybdate, weighed in this form or as magnesium pyrophosphate after precipitation with magnesia mixture in ammoniacal solution. Manganous oxide is determined colorimetrically after oxidation to permanganate. See also under (6).

6. To avoid the necessity of proportional division of the solution obtained from the former sample (5) phosphorus can alternatively be found in a separate sample by the same treatment. In this case it is profitable to decompose the sample in which manganese is to be determined with a mixture of sulphuric and hydrofluoric acids.

7. The presence of carbon dioxide even in very small amounts can be detected by adding hydrochloric acid to the cold, previously boiled suspension of the rock powder in water. The test-tube should be inspected with a lens for minute bubbles and a lead acetate paper placed in the opening of the tube ensures that hydrogen sulphide is not mistaken for CO_2.

In the case that carbonates prove to be present in appreciable quantities, the determination is called for and any of the well known apparatus may serve for this purpose.

8. If it is desired to determine by chemical methods any of the enumerated metals or sulphur in either state, this may be done in a very convenient way in one sample by HILLEBRAND's method. The powder is fused with sodium-, or in this case preferably, potassium carbonate, some nitre being added to oxidise sulphide sulphur. The cake is decomposed in water and in the acidified liquid, the sulphate is precipitated with barium chloride. The insoluble residue is treated with sulphuric acid; the barium sulphate thus obtained is purified and weighed. Zirconia is precipitated in the filtrate from barium sulphate with phosphate, titanium being kept in solution with hydrogen peroxide. In the filtrate from the zirconia determination, the rare earths are precipitated together with iron and titania by sodium hydroxide solution and separated as insoluble fluorides. Chromium may be estimated, in the aqueous extract of the fused cake colorimetrically or this may be done in a separate portion by the same procedure.

9. Further constituents, for example SO_3 Cl, F, NiO, CuO, BeO, B_2O_3, V_2O_5 etc. might be found in other, usually larger, portions by special methods, their determination may become of prime importance in the analysis of minerals and will be treated in a further section.

DECOMPOSITION OF SILICATES.

Various silicates are easily attacked by concentrated mineral acids *either direct or after fusion or sintering*. This may be applied in mineral analysis even for quantitative separations. For rocks the method ordinarily proves to be unsatisfactory, but one may have recourse to it for so-called rational analyses where the amount of a given soluble mineral is to be recorded. In this case the sample should be prepared in the same way as the portion for the determination of the alkalies, namely extremely fine. This procedure may be used also to keep the amount of alkali salts in an analysis low, by fusing only the *residue* of an acid extraction with fluxes e.g. sodium carbonate, provided a considerable part of the sample is soluble in the acid employed.

The decomposition with acids will preferably be done at ordinary temperature to avoid rendering the silica insoluble. If heating is employed directly, the silica that is liberated by the acid would separate on the mineral fragments and protect them for further attack whilst in the former case only a hydrogel is formed, permitting diffusion.

Only very few minerals resist attack by hydrofluoric acid; consequently a specially prepared pure HF is used in silicate-analysis for various decompositions e.g. for the determinations of ferrous iron, manganese and phosphorous pentoxide. Silica cannot be determined after a decomposition with HF, except when a very expensive Pt-apparatus is available. If this attack is used in determinations of sesquioxides complete elimination of fluorine is required as this element interferes with the precipitation of aluminium (making the separation incomplete) and with the colorimetric comparison for titania. Either HF or sulphuric acid cause trouble when calcium is present in large amounts. Complete elimination of HF is obtained by heating with sulphuric acid until copious fumes are given off, then diluting with a few ml of water *after cooling* and again warming till

fumes appear.

Decomposition by fluxes is widely applicable. The main portion is generally fused with sodium carbonate or alkali hydroxide. [24]) If the latter is used a nickel, silver or gold crucible has been recommended. Nickel and silver are objectionable; platinum crucibles are attacked severely by fused caustic alkalies. A *palau* crucible is convenient, but I do not prefer this method as alkali hydroxides are apt to be contaminated with foreign matter more readily than carbonates and the fusion is difficult to carry out in an "analytical" manner.

For alkali-determinations according to the method of LAWRENCE SMITH the silicate is decomposed with CaO and $CaCl_2$. In the same portion total iron and silica can be checked. [25]) Other fluxes have been described e.g. calcium sulphate, pyrosulphates, calcium-, lead- and boron-oxides, ammonium fluoride etc. and may be valuable in particular cases but the *"communis opinio"* is against them and in general they are indeed liable to serious objections.

For the main portion, fusion with alkali carbonate followed by digestion with hydrochloric acid is usually the most convenient method of bringing a *mixture* of silicates into solution. As larger quantities of potassium salts are carried down in precipitates — especially in the ammonia precipitate and with magnesium — than sodium salts, sodium carbonate should be used; the application of a mixture of soda and potash is very objectionable in this case. A palau crucible is preferable according to WASHINGTON, but one of platinum, if not dented, will serve also.

PROCEDURE FOR SODA FUSION.

The clean crucible is heated and placed for 10' in the open balance. An amount of 0.5—1.0 g of rock powder (say *a* gram) is weighed out accurately. About 1.0 g is advisable for rocks with 70 % silica and with decreasing silica-content the amount of powder should be reduced to 0.5 g for 40 %. With these quantities precipitates will be of a convenient size.

Next a pair of filter papers is placed on the balance pans and $(5 \times a + 2)$ g of anhydrous sodium carbonate is weighed out to 0.1 g. Most of this is carefully added to the rock powder in

the crucible and *intimately* mixed with it, with the aid of a thin glass rod or platinum spatula, previously somewhat warmed. The rod or spatula is dry-washed with the rest of the soda and this is poured evenly on the mass in the crucible.

The crucible is placed above the 3 cm flame of a BUNSEN burner and the heat is very gradually increased, until the carbonate begins to melt. The crucible is kept at this temperature for some time as the reaction will then proceed without much spluttering and the carbon dioxide is driven off safely. The crucible should not be enveloped wholely by the flame, an oxidising atmosphere within it being necessary to prevent reduction of some iron oxide into the metallic state. This iron would form an alloy with, and harm the metal crucible, besides escaping determination. Therefore, if the full heat of the burner is employed, the latter should be clamped in a direction making an angle of at least 45° with the vertical. These inconveniences are avoided by using an electric furnace. The crucible is placed in it when cool and the current is switched on. By either of these methods it is quite well possible to assure complete decomposition without excessive spluttering on the crucible lid. Acid rocks yield a clear mass; however if much iron, magnesium and calcium are present, the liquid will be turbid. On cooling no "volcanoes" should form as this indicates that decomposition has been incomplete. In this case higher temperatures or longer fusion are required and *if need be* a few more grams of soda may be added to obtain a fluid and not merely a half molten or sintered mass. This last will seldom be necessary.

Ordinarily the cooled mass is of greenish colour due to sodium manganate and the amount of manganese may be estimated by this colour.

In powerful electric furnaces, soda-fusions in platinum crucibles should not be prolonged unduly as caustic alkali is formed by dissociation of carbonate and the crucible may easily lose from 2.5 to 10 mg and more in weight. Palau crucibles are therefore preferable.

By gentle tapping on the bottom of the crucible the melt ordinarily separates quite readily from it. Distortion, however, is strictly to be avoided. Rotating the fluid mass to obtain a larger surface is unnecessary and causes closer adherence of the melt to the wall, whilst too rapid cooling will be injurious to the crucible. The best way of cooling is placing the crucible on

a flat polished stone surface. If this procedure proves to be ineffective the crucible is half filled with water and gently heated. The mass now certainly frees itself, the water penetrating between the fused cake and the walls.

The cake is transferred to a platinum basin or silica-glass dish of at least 400 ml capacity. For most work I prefer fused silica, not only for its low cost, but also because platinum is likely to be dissolved in the evaporation of the liquid. Good quality "quartz" dishes are rather constant in weight even over long periods and *silica only* will be affected by a slight error which moreover tends to be compensated and is altogether unimportant, whereas for the attack of platinum, corrections ought to be made. If a platinum basin is used, the melt should disintegrate wholely in water, a few drops of pure alcohol, preferably methanol, are added to destroy any manganate and only then hydrochloric acid may be introduced. Attack of platinum by ferric salts or by combined action from HCl and oxygen from the air cannot be avoided during the evaporations. New porcelain dishes may be used for all but the most accurate work a few times until the glaze becomes cracked whilst glass is unsuitable for this part of the analysis.

The spots on the lid of the crucible are washed with *water* drop by drop into the crucible. The solution of the residual parts from the cake is effected in the crucible and this liquid is poured into the basin. The lid is next rinsed with HCl 1 : 2 and the crucible with this liquid is put aside. This order prevents silica adhering strongly to the walls of the crucible as it is loosened in the form of water-glass.

The basin is covered with a watch-glass (concave side upwards) of resistance-glass. An excess of dilute hydrochloric acid (1 : 1) is introduced cautiously with a pipette under the lid. This will dissolve the cake gradually and for the reason mentioned under "attack by acid" this should take place at ordinary temperature. When the effervescence ceases, the contents of the crucible are added and larger masses of colloidal silica are broken up with the platinum spatula or a glass rod. The crucible is washed with water, heated and weighed. The loss rarely exceeds 0.1 mg provided the above precautions are taken.

The complete disintegration of the cake should be waited for and it is useless to try hastening this procedure; by heating, the opposite effect is reached, whilst mechanical operations are likelv to cause losses.

Dehydration and Separation of Silica; General Considerations.

The liquid in the dish still contains some silica in solution, whilst the remainder occurs as floating particles. To effect the separation of the silica in an insoluble granular form it has to be dehydrated and therefore the liquid is evaporated repeatedly with alternative filtrations. Double evaporations without intermediate filtration do not yield better results than one single evaporation and are a mere waste of time. Silica is contaminated ordinarily with elements belonging to the ammonium hydroxide group and also with calcium sulphate in the case of the rock containing much calcium together with sulphide or sulphate.

In a number of analyses the first and second precipitates were examined separately. In general the second evaporation yielded 0.4—0.5 %, rarely 1.0 % of the amount of silica. Third evaporations in platinum basins yielded only a few tenths of a mg in three determinations. According to authorities like HILLEBRAND and WASHINGTON some silica remains in the liquid and cannot be obtained even by further treatment in the same way. This silica is coprecipitated with the sesquioxides; however, the correction for silica in the ammonia precipitate, should only be applied if at all, to get exact values for alumina as most of it is brought into the analysis by attack of the beakers and cannot be presumed to have been part of the rock sample. The silica from the second evaporation is very impure; in a basaltic rock I once found 3.6 mg impurities to 1.1 mg silica, whereas the first portion contained only 0.0052 g to 0.2710 g silica. In washing the silica obtained by the evaporations, extreme care should be taken completely to remove the alkali salts as these give rise to serious errors in the determination.

Boron as well as fluorine, if present in large amounts, interferes with the determination of silica, but it is not likely that these will occur in ordinary rocks in such quantities as to influence the results appreciably. So the procedure for the determination of silica, boron and fluorine, if simultaneously present in one sample, is dealt with in the chapter on silicate-mineral-analysis.

PROCEDURE FOR THE DETERMINATION OF SILICA.

The liquid is evaporated in the dish. When salts begin to appear, the crust should be frequently broken up and the mass stirred with a thin glass rod or stiff platinum wire. When apparently dry, complete dehydration may be promoted in an effective way by adding 5—10 ml pure alcohol, the pasty mass being stirred until most of the liquid is evaporated. This causes a slight increase in the weight of impurities, probably due to hydrolysis, but this is unimportant. Drying at higher temperatures, than those that may be reached with a vigorously boiling water-bath, are to be avoided as this leads to formation of acid soluble Mg-silicates and consequently causes low results for silica. After the mass is substantially dry, the dish is allowed to cool, just enough hydrochloric acid, 1 : 1, is added to moisten the mass and one quarter of an hour is given, so that the acid may act on the hydroxides formed by hydrolysis, as completely as possible. After this time the salts are taken up with just enough hot water. The liquid is then decanted through a quantitative filter (9 cm); gentle suction will be advantageous. After the third decantation with water containing 5 % HCl the silica is brought on the filter by a jet from the wash-bottle; the stirrer and the dish are cleansed with a little piece of moist filter paper, the filtrate is poured into the dish and evaporated for the second time. Meanwhile the silica is thoroughly washed free from alkali-salts and other impurities with water, until chlorine proves to be absent in a test with silver nitrate on a few drops of the washings. This filtrate is to be reserved.

After the second evaporation the mass in the dish is treated in exactly the same way as was described above, but the salts are to be dissolved in the reserved filtrate. For the second filtration a filter from 5 or 7 cm will be large enough. This precipitate is also duly washed until free from soluble matter.

The first filter is placed in the second one; the precipitate is wrapped up in the paper and the whole is transferred moist to a previously ignited and weighed platinum crucible. The filter is carbonized and ashed at as low heat as is possible and special care should be taken to prevent the ignition of the escaping gases, as this unavoidably causes loss of the very fine silica-powder. The operation takes some time and should not be hastened. When the whole mass is white, the temperature is

raised and the final ignition has to be done in 5—10' with the blast, during which the crucible is tightly covered by the lid. The crucible is cooled in the dessicator and weighed as soon as is possible to prevent attraction of water by the somewhat hygroscopic silica. Re-ignition is necessary until constant weight is reached.

The silica is moistened with water. To prevent loss of the light powder the tube of the wash-bottle should be filled completely and the drops directed on the wall of the crucible. 5 drops of sulphuric acid, 1 : 1, are added to prevent volatilisation of titania as fluoride and enough pure 40 % hydrofluoric acid is added to drive away the silica. This operation should be carried out under a separate hood with powerful draft. Finally the sulphuric acid is evaporated by waving a low flame gently round the crucible and completely expelled by adding two or three times small grains of pure ammonium carbonate, immediately covering the crucible and proceeding to heat. This heating should not be too long, neither should the temperature exceed 800—900°, lest some alkali-salts (if the washing has been incomplete) or tungsten-compounds (if present) may volatilize.

The crucible with the impurities from the silica is weighed. The difference from the former weighing gives the exact amount of silica in the precipitate. Finally the impurities are fused with about thirty times their weight of sodium carbonate, the melt dissolved in hydrochloric acid, *the carbon dioxide thoroughly expelled* and the solution which may be turbid (due to titania and zirconia) is added to the filtrate from the silica. The mass of the crucible is checked. If the impurities are milky white at ordinary and yellow at high temperature this indicates the presence of much titania or zirconia or both.

HYDROGEN SULPHIDE GROUP.

The determination of elements belonging to this group will rarely be required. I therefore refer, for the methods, to the chapters on the analysis of carbonates and of ore-minerals. Spectrographic methods are appropriate here. It should be noted that small amounts of copper may originate in the still or may be caused by slight contamination due to the water-bath, whilst platinum metals or gold may have been introduced by the crucible etc. *Metal-wire sieves are inadmissible* in preparing

the sample when the hydrogen sulphide group is to be determined. After precipitations by means of this reagent the excess of it should be expelled and ferrous iron re-oxidised to the trivalent state, preferably by boiling with enough saturated bromine-water followed by expulsion of the excess of bromine.

AMMONIUM HYDROXIDE GROUP, GENERAL CONSIDERATIONS.

The next step in the analysis of the main portion is the precipitation of a large number of elements in the form of their hydroxides by adjustment of the hydrogen-ion-concentration. Ammonium hydroxide is most suitable as no nonvolatile substances are introduced into the liquid and the conditions can be arranged so as to give complete separation from alkaline earths, alkalies and almost all the manganese (also nickel and zinc if present). In the case of manganese, the alternative is to coprecipitate it wholely with the sesquioxides according to the procedure worked out by BLUM by oxidizing manganous salts to the dioxide. [26]) BLUM has given also the conditions for preventing this coprecipitation as much as is possible and LUNDELL proved these conditions to be satisfactory even if unusually large amounts of manganese were present. The original text is as follows: [27])

> "To the solution containing 5 g of ammonium chloride per 200 cc solution, or an equivalent amount of hydrochloric acid, add a few drops of methyl-red (5—7) and heat just to boiling. Carefully add dilute ammonium hydroxide dropwise until the colour of the solution changes to a distinct yellow. Boil the solution for 1 to 2 minutes and filter at once. Wash the solution thoroughly with hot 2 % ammonium chloride or nitrate solution".

The once very common basic-acetate method is rather tedious, and as the results reported by LUNDELL show that ammonia is quite satisfactory, even in silicate analysis, the old method may as well be abandoned.

Fluorine should be absent, otherwise precipitation of aluminium will be incomplete. (p. 40) Boron likewise causes troubles here as it cannot be completely removed from the ammonia precipitate even by three precipitations (p. 115).

The hydroxides are divided into two groups by double precipitation with sodium hydroxide solution. If this reagent —

now available in very good quality (*e natrio*) — is added in slight excess, aluminium, phosphorus, vanadium, beryllium, gallium, germanium and others go into solution; iron, titanium if much iron is present, zirconium, rare earths and chromium are precipitated, whilst uranium divides. Chromium, vanadium and uranium may be kept in solution by oxidising with hydrogen peroxide.

In rock analyses, the preponderating elements in this group are iron, aluminium, titania and phosphorus, perhaps in some rocks also zirconia and beryllium. Titanium is determined in the joint precipitate with iron by fusion with potassium pyrosulphate followed by colorimetric comparison, whilst phosphorus can either be determined in the aluminium-precipitate or better in a separate portion of the rock sample. If properly carried out, this procedure is quite satisfactory, especially because aluminium need not be determined by difference (but for the small quantity of phosphorus) and this is to be preferred, as the true amount of aluminium is of prime importance in petrological discussions and formerly many determinations with other methods were inaccurate.

PROCEDURE OF PRECIPITATION WITH AMMONIA.

The proper conditions for the precipitation with ammonia are well known now, as was pointed out above. To prevent co-precipitation of magnesium, an excess of ammonium salts should be present, thus avoiding coming within the range of hydroxyl-ion-concentration which will cause separation of this element.

This "buffering" serves equally for obtaining correct values for aluminium, which will be precipitated completely at pH-values from 6.5—7.5 whilst re-solution of the aluminium hydroxide — occurring at higher pH — will be largely overcome. Ammonium salts in the wash-water prevent turbid washings by their flocculating power. Complete separation from alkaline earths and magnesium is generally obtained by double precipitation, but for high percentages of magnesium, the operation should be carried out three times in the same way. Obviously the ammonium hydroxide should be as freshly distilled as possible and carbonate must not be present in it, otherwise separation from the alkaline earths will be incomplete.

From 5—15 ml concentrated hydrochloric acid are added to yield sufficient ammonium chloride in the liquid (the solid salt being generally impure) and also a few drops of methyl-red solution. The liquid is heated just to boiling and dilute ammonium hydroxide is added until the colour is distinctly yellow (visible when the precipitate has settled somewhat). After this point is reached, a few more drops of the precipitant are added until a slight and by no means disagreeable ammoniacal odour is produced, *which must not disappear on stirring.* The air in the beaker is to be waved about with the hand to prevent contamination with carbon dioxide from the breath. The suspension is boiled for 1—2', filtered (11 cm) directly without suction and washed two or three times with a hot 2 % ammonium chloride solution, fresh liquid being added only after complete draining of the filtrate.

With the aid of platinum-tipped tweezers the filter is raised cautiously to allow the liquid in the stem to flow into the beaker below the funnel. Next the funnel is held in a nearly horizontal position over the beaker used for the precipitation with ammonia and with a fine jet of *water* from the wash-bottle the hydroxides are quantitatively rinsed back into the original beaker. It is essential that the hydroxides to be re-dissolved are rinsed into the beaker with *water* as only iron hydroxide readily dissolves in hydrochloric acid and small amounts of the other hydroxides may be overlooked on the filter paper when deprived of their iron-content. The funnel with filter is replaced in the stand and may serve directly for the second filtration.

The hydroxides in the beaker are re-dissolved by boiling with 10—20 ml hydrochloric acid, 1 : 1. After diluting to 100 ml, the hydroxides are re-precipitated in exactly the same way as has been described and with excessive amounts of magnesium present in the rock, the procedure should be repeated once more; in the last filtration 8—10 portions of wash-liquid should be used. The filtrates are united in one 600 ml beaker and are reserved for the determination of (manganese,) calcium and magnesium.

The hydroxides are again dissolved in a minimum of acid and the precipitation is now to be carried out with a freshly prepared 10 % NaOH-solution. At the equivalence point, the colour depends on the ratio Al: Fe in the precipitate; with some excess, a *sudden change* to dark-brown is observed, indicating that

soluble sodium aluminate has been formed. Instantaneous filtration from the hot liquid, again through the same filter, is followed by two or three washings with warm 2 % NaOH-solution and then the precipitate is rinsed back into the beaker, dissolved in hydrochloric acid and the whole operation is repeated to free the precipitate from traces of aluminium and phosphorus. Both filtrates are united in one 400 ml beaker and are reserved for the determination of aluminium and phosphorus. The precipitate is thoroughly washed, at first a few times with warm 2 % NaOH-solution and then with water. The filter is raised cautiously with platinum-tipped tweezers, opened over the original beaker and the precipitate is rinsed with a fine jet of water from the washbottle into this beaker and is dissolved in hydrochloric acid. The filter is macerated by vigorously shaking with a small volume of water in a small Erlemeyer flask (150 ml); this will cause no difficulty as the strength of the paper has been diminished by the various operations. If for this reason the filter is considered to have been weakened too much *in the meanwhile,* it should previously to possible puncture be substituted by another smaller filter (7 or 9 cm) and both filters will be macerated in this stage. One should, however, try to avoid this, as too much filter paper pulp causes difficulties in the subsequent filtration and ignition of the precipitate.

The separation of the ammonia precipitate into two groups is now complete: iron and titania are in hydrochloric acid solution in the original beaker, while aluminium, phosphorus and the like are in alkaline solution in the 400 ml beaker. The latter liquid is *at once* neutralised with concentrated HCl (to avoid possible attack of the glass by the alkaline solution) the beaker being kept covered to prevent loss by spluttering. A precipitate of aluminium hydroxide will appear and re-dissolve in a slight excess of acid. Iron and titanium are precipitated in the other beaker by adding sufficient ammonium hydroxide to produce a pronounced ammoniacal odour. An excess will do no harm in this case; titania, will not be precipitated — at least in such a form as to be retained by the filter — if there is insufficient iron; this case is, however, improbable in naturally occurring materials as the titania content is usually correlated to the iron-percentage. Finally the precipitate is intimately mixed with the macerated filter paper; this makes filtration easy and causes a finely divided state of the mixture of oxides after ig-

nition, this being convenient for the further attack with molten pyrosulphate besides promoting the re-oxidation of any magnetic oxide (Fe_3O_4) that may have formed during the charring of the paper. The macerated filter paper with the precipitate is filtered off on a paper of 9 or even 7 cm and the whole is washed thoroughly with hot 2 % ammonium nitrate solution until chlorine is absent in the filtrate. *This filtrate is rejected.* Then the filter is carefully sucked dry and placed in a previously ignited and weighed platinum crucible. Filter and precipitate are ignited cautiously, a final temperature of 900 or 1000° being amply sufficient completely to expel all the water. The ignited oxides are not hygroscopic. In the mixture, titanium is to be determined after fusing with pyrosulphate and dissolving the melt resulting from this operation; see under titania (p. 52).

The solution containing aluminium and phosphorus is to be treated in exactly the same manner as has been described in this section for the whole ammonium hydroxide group. So an excess of ammonia is to be avoided and double precipitation will be necessary to remove the sodium salts. After the final precipitation some filter paper pulp is added and the whole mass in the beaker is filtered off and washed thoroughly (10—12 times) with a hot 2 % ammonium chloride solution. When non-volatile matter proves to be absent in the filtrate (test on piece of platinum foil) the washing may be considered to be complete and the precipitate is cautiously sucked dry.

The filtrate from the first of these two filtrations is tested for the absence of calcium and magnesium as described in the chapter on the determination of these elements. The second filtrate may safely be rejected. Macerated filter paper should not be added before the final precipitation is complete, lest the filter paper fibre be impregnated with aluminium hydroxide; as this tends to make it fireproof the ignition will be difficult to carry out. The precipitate is wrapped in the filter and placed moist in a platinum crucible. Aluminium oxide is usually extremely hygroscopic, but loses this inconvenient behaviour when heated for a short time to 1200°, owing to the formation of α- Al_2O_3 or corundum. This temperature is obtained in platinum with a good blast. Heating to 1200° or even more is incompatible with simultaneous determination of iron, as magnetite, Fe_3O_4 is likely to be formed and hence the amount of iron found will be too low. The aluminium precipitate should be ignited until

constant weight is reached.

Phosphorus may be determined in this precipitate after fusion with soda, the rest of the operations being carried out as described under the methods of determination of this element. The separation of beryllium from aluminium and phosphorus will be dealt with in the chapter on mineral analysis as beryllium is not likely to be found in rocks in quantities warranting even its detection.

CALCULATION OF THE SESQUIOXIDES.

The amount of phosphorus is to be deducted from combined phosphorus and alumina to yield the exact amount of the latter. In the same way total iron will be found as the difference of the combined oxides and titania. The correct value for iron, however, can only be given after the determination of ferrous iron, lest a surplus of oxygen may raise the sum, besides making the analysis inaccurate with regard to the state of the iron. If still other elements of this same group are present, their amounts should be subtracted from the percentage of Fe_2O_3, or Al_2O_3.

DETERMINATION OF TITANIUM (AND ZIRCONIUM).

This element is determined in the combined oxides of iron and titanium as follows: to the crucible containing the oxides, 3—4 g of potassium pyrosulphate are added and the whole is placed over the small flame of a Bunsen burner at such a height that the salt just melts. Small amounts of water are driven off without loss by spluttering if this part of the fusion is done cautiously, without hurry and under cover. The heat may be gradually increased owing to the evaporation of sulphur trioxide causing the melting-point to rise and finally the process is terminated in a few minutes by taking the crucible in a pair of BLAIR's tongs, carefully rotating it to catch all of the precipitate and increasing the heat until no solid particles remain. At high temperatures the liquid is very dark, but complete solution of the precipitate can easily be established either in the case that the crucible is hot enough for the bottom to become dull red or by observing in strong daylight while cooling the

liquid. The colour diminishes gradually and a few moments before the appearance of the crystal crust the liquid is only slightly yellow and the bottom may be inspected conveniently, This fusion should not be prolonged unduly, neither should the temperature be higher than necessary as pyrosulphate fusions attack platinum (and alloyed crucibles) considerably. The crucible, however, is cleansed very effectively.

The cake separates readily from the crucible and is brought into solution in dilute sulphuric acid (at least 10 % sulphuric acid by volume). Titanium is determined colorimetrically in this solution by Weller's method. 3 % Hydrogen peroxide is added until the colour does not deepen on further addition of the reagent. The liquid is compared with a standard solution, either in a DUBOSCQ colorimeter or some similar pattern or in a colorimeter of the type advocated by HILLEBRAND, being a modification of the WELLER form, or by comparison with a scale, made by subsequent dilution from the standard solution. The mixture should preferably contain amounts of from 1.5—20.0 mg titanium dioxide in 100 ml and the comparison is best done more than once under different conditions e.g. more or less diluted. The values thus obtained should lie close together (± 5 %). The procedure of colorimetric comparison is given in the chapter "Operations" and need not be repeated here. For low amounts of titania the results are even more accurate than those obtained by gravimetric methods. The latter are obviously preferable for larger quantities and will be dealt with in the next section.

Zirconium may be determined, after the colorimetric determination of titanium, in the same liquid by precipitation as zirconium phosphate as described on p. 101. The colorimetric comparison for titanium should be made *before* the addition of phosphate because of the bleaching effect of phosphates on the yellow colour.

The separation of the ammonia precipitate yielded two filtrates, one resulting from the first two filtrations, the other from the purification of the "aluminium-group". Both filtrates may still contain small amounts of sesquioxides; these can be recovered by concentrating the slightly ammoniacal solution, preferably in platinum basins, filtering off any hydroxides which may separate and determining, their weight as oxides. If, however, the precipitations with ammonia have been carried out adequately this correction will be insignificant and when

large enough platinum basins are not available the whole operation is better omitted. The recovered oxides may be evenly distributed among iron and alumina.

OTHER METHODS OF SEPARATION FOR THE ELEMENTS OF THE AMMONIA PRECIPITATE.

The procedure advocated by WASHINGTON and HILLEBRAND is as follows: [28])

The filtrate from the silica is treated in the same way as has been described, but after the second precipitation with ammonia the macerated filter paper from the first filtration is added, the whole placed on a new large quantitative filter (11 or 12½ cm) and duly washed 12—16 times with hot 2 % ammonium nitrate solution. A positive chlorine reaction in the last filtrates necessitates further washings. The filter is sucked dry as completely as possible, placed moist in a weighed platinum crucible and is carefully ignited. Any hydroxides recovered in the filtrate by evaporating down the latter are added to the main mass of the ammonia precipitate before ignition. The temperature should be as nearly as possible 1200° in the final ignition. The weight of the *combined* hydroxides is reported. In the same crucible a fusion with potasium pyrosulphate is made as described under the determination of titania. The dilute sulphuric acid solution of the melt is evaporated down to fumes to recover the residual silica. This silica is almost always derived from the glass apparatus used in the precipitation of the sesquioxides. Only in the case that platinum apparatus has been used exclusively throughout the whole operation until this step, is this silica added to the main silica. Therefore (and otherwise to apply a correction to Al_2O_3) the precipitate is filtered off, ignited and the loss in weight after a treatment with hydrofluoric and sulphuric acids (a few drops of each of them will be enough) represents the recovered silica, belonging either to the main silica or being merely a contamination of the aluminium oxide.

Iron is determined in the filtrate titrimetrically with potassium permanganate solution after reduction with hydrogen sulphide and expulsion of any excess of this reagent in a stream of carbon dioxide. Zinc is generally unsuitable for this operation, titanium being reduced to a trivalent compound. A correction

for this cannot, however, be safely applied. For this question the reader may consult the manuals on titrimetric analysis.

PROCEDURE FOR THE REDUCTION OF IRON BY HYDROGEN SULPHIDE.

Fuse the residue obtained after the volatilization of the residual silica with a small lump of potassium pyrosulphate, dissolve in a little water and add the solution to the filtrate from the residual silica. This will be in a beaker and is diluted so as to make the concentration of free acid from 1.5—2.5 % by volume. Hydrogen sulphide is introduced in a gentle stream and will reduce iron alone (with separation of colloidal sulphur) and precipitate platinum, originating mostly from the fusion with pyrosulphate and also from the evaporation with hydrochloric acid — in the determination of silica — when this has been carried out in a platinum basin. The advantage of hydrogen sulphide over zinc is, that it does not reduce titanium and over sulphur dioxide that it also precipitates platinum; otherwise the latter metal would be reduced to the bivalent condition and afterwards consume an equivalent amount of potassium permanganate solution. The complete precipitation of platinum and the separation of sulphur in an easily filterable form is obtained by gradually increasing the temperature with continuous passage of the gas until the boiling point is reached. The slightly cooled solution is filtered quickly through a small filter into an ERLEMEYER flask (500 ml). Hydrogen sulphide is again introduced to reduce any iron that may have been re-oxidized during the filtration. Pure carbon dioxide is next introduced (free from hydrogen sulphide and oxygen; a cylinder of the liquefied gas or else a Kipp-generator may be used; wash-bottles with copper sulphate and pyrogallol.) The solution is again heated to boiling and cooled in the *increased current* of the gas when — by testing with lead acetate-paper — hydrogen sulphide proves to be absent. The cooling is hastened by placing the flask in a dish with ice cold water. Directly after cooling, the solution is titrated with standard permanganate solution. The strength of this solution should not exceed the equivalent of 2.5 mg of iron to the ml or about 1/30 N.

On the addition of hydrogen peroxide to the solution after titration, titanium shows its presence by a yellow colour. This

solution, diluted or concentrated when necessary, may be used for the colorimetric comparison for titanium (p. 52). For every 1 % of titanium in the substance the total volume may be increased by 100 ml.

The filtered platinum sulphide and sulphur is ignited in a small porcelain crucible and the weight of the metallic platinum determined. If this weight exceeds the loss in weight of the crucible used in the pyrosulphate fusion, the excess will have been derived from platinum apparatus previously used and must be subtracted from the total weight of the ammonia precipitate. Ordinarily this correction will not be necessary.

ALTERNATIVE METHODS FOR THE DETERMINATION OF THE SESQUIOXIDES ETC.

Various other methods have been suggested for the separation and determination of elements belonging to the ammonium hydroxide group. These methods may be divided as follows:

1. The group separation is carried out with ammonium hydroxide but the separation of the elements of the group is made according to other methods than those described in the above two procedures.
2. The *group separation* is effected with other reagents.

These procedures were in general intended by their authors for special purposes. Consequently, only a brief description of the most important among them will follow here, so that the analyst may decide whether or not any of these methods may be applicable with advantage in carrying out the analysis of a definite compound. More attention will only be paid to one of the procedures belonging to the first group, namely the separation of titanium from iron (and aluminium) followed by the gravimetric determination after precipitation with cupferron. This method is very important for the analysis of compounds with large percentages of TiO_2, as in this case the colorimetric determination of this element would yield inaccurate results

1a. JANNASCH and DITTRICH [29]) recommend the separation of the ammonium hydroxide group by fusion with sodium hydroxide in a silver crucible (potassium hydroxide attacks silver crucibles more than the sodium compound when molten. This method is not to be recommended as much larger quantities of

sodium hydroxide are required than with the procedure described on p. 49 and the volume of liquid is consequently much larger, the fusion is tedious to carry out and the contamination of the precipitates with silver must be allowed for afterwards, lest the results become inaccurate and the platinum crucible be damaged by the formation of an alloy with the metallic silver. The further separation after solution of the cake is governed by the same principles as have been described in the former methods. A gold or palau crucible is preferable to one of silver; for less accurate work a nickel crucible will even be applicable.

1b. It is also possible to make the same separation by fusing the precipitate with sodium carbonate or with a mixture of sodium carbonate and borax. [30]) Beryllium will in this case accompany iron and the like. [31]) Owing to the formation of soluble sodium ferrite, which will not be decomposed directly when dissolving the melt, the precipitation of iron will be incomplete, about 1 % of this metal remaining in solution. A suitable procedure in this case is to dissolve the melt in water, the solution being promoted by warming on the water-bath; after digesting for a time at 60—70° with a few ml of ethanol and after the addition of two grams of pure solid sodium hydroxide, the solution is filtered off from the residue. The whole operation should be repeated with the residue, otherwise the separation of aluminium will be incomplete.

1c. With cupferron, iron, titanium, zirconium, vanadium and part of the rare earths are precipitated, the other elements remain in solution. [32])

1d. Electrolysis with a mercury cathode removes iron and chromium from the solution, while the other elements remain unaffected. [33]) Electrolytic procedures will be described in the chapter on ore analysis. The method is particularly useful when very small amounts of aluminium are present together with much iron, for example in the analysis of extremely "basic" rocks (peridotites or dunites, etc.).

1e. Very good results may be obtained by the separation of iron as sulphide in ammonium tartrate solution and subsequent precipitation of titanium with cupferron. The precipitate is ignited and weighed as TiO_2; iron is determined as oxide after expulsion of the hydrogen sulphide and aluminium may be estimated in the filtrate of the cupferron precipitate or by difference.

PROCEDURE FOR THE GRAVIMETRIC DETERMINATION OF IRON AND TITANIUM.

The ammonia precipitate is ignited moist as already described and the weight determined. After fusion with pyrosulphate, the residual silica is ascertained and the solid residue after evaporation of this impure silica with hydrofluoric and sulphuric acids is fused again with some pyrosulphate and the solution of this melt added to the filtrate from the residual silica. (p. 54)

Tartaric acid (about four times the weight of the combined oxides) is dissolved in this liquid. The solution is made up to 1 % by volume of sulphuric acid (by careful neutralization followed by the addition of the required amount) and the iron is reduced to the bivalent condition by the introduction of hydrogen sulphide until the solution is colourless. This is necessary to prevent the precipitation of ferric sulphide which would co-precipitate titanium in spite of the addition of tartaric acid. After complete reduction of the iron, the solution is made distinctly alkaline with ammonium hydroxide and the introduction of hydrogen sulphide is continued. When the precipitation of ferrous sulphide is complete, time is given (the beaker or flask being covered) for the precipitate to settle; next the sulphide is filtered off, and washed thoroughly with water containing ammonium sulphide and another ammonium salt. The filter and precipitate are transferred to a clean beaker and the precipitate is dissolved in hydrochloric acid, 1 : 1, the paper is pulped by vigorous stirring and after expulsion of the hydrogen sulphide by boiling, a few drops of bromine water or concentrated nitric acid are added to oxidize the iron and the metal is precipitated with ammonia in excess. After filtration, the hydroxide is converted to oxide by ignition.

Only THORNTON's method for the gravimetric determination of titanium will be described as the other available methods require the destruction of the tartaric acid and sometimes the preparation of a hydrochloric acid solution instead of a sulphuric acid solution. [34])

To the filtrate from the iron sulphide are added about 40 ml of sulphuric acid, 1 : 1, and the liquid is boiled until hydrogen sulphide is completely removed. The solution is quickly cooled under the tap, diluted to 400 ml and with constant stirring, titanium is precipitated by the gradual addition of a 6 % cold

solution of cupferron in water. When the precipitate has settled somewhat, the supernatant liquid is tested with a few drops of the reagent to determine whether the precipitation was complete. This further addition should yield a white precipitate whereas the required precipitate is yellow. The precipitate is filtered off on a paper filter in a platinum cone with gentle suction. After washing the precipitate with twenty portions of dilute hydrochloric acid, 1 : 10, filter and precipitate are sucked dry as far as possible, and dried in a platinum crucible at 110° in an oven.

The crucible is nearly covered with the lid and the ignition is commenced with a *very small flame* under the hood. Heavy smokes are liberated and gradually the height of the flame may be increased. The lid is removed from the crucible and freed from adhering carbon by burning the latter away and the same is done with the carbon in the crucible. The covered crucible is next heated and the weight of the titanium dioxide determined. After fusion with potassium pyrosulphate, the operation is to be repeated to free the titania wholly from alumina.

Zirconium will be determined separately and should be deducted from the percentage of titanium here obtained.

Vanadium is partly co-precipitated, if present at all, and may be removed by fusion with sodium carbonate, whereby it goes into solution whilst zirconium and titanium remain undissolved after extraction of the melt with water.

Aluminium is determined by difference.

In view of some difficulties in the method described it is desirable to mention the possibility of a convenient determination of titanium, zirconium and aluminium in the filtrate from the iron-sulphide, provided the rare earths are absent.

The filtrate is evaporated down as far as possible in a platinum basin and is heated with 10—12 ml of concentrated sulphuric acid. After cooling add 5 ml of fuming nitric acid and again heat until the organic matter is oxidised. The metals present and phosphorus — as far as the latter constituent has not been removed by the evaporation with sulphuric acid — are precipitated with ammonia and after ignition, the precipitate is fused with sodium carbonate. After extraction of the melt with water, titanium and zirconium remain undissolved as sodium compounds; aluminium is precipitated together with the remainder of phosphorus and is weighed after ignition. As part of the phosphorus will have been removed in the course of the analysis, a

correction for the whole percentage of phosphorus present in the sample would be incorrect, though the matter is of little importance with small percentages of P_2O_5. Otherwise the phosphorus content of the aluminium precipitate should be determined according to the molybdate method after fusion of the precipitate with sodium carbonate in the *nitric* acid solution of the melt.

Still other methods for the separation of the elements of the ammonium hydroxide group exist, e.g. sublimation of iron in a current of dry hydrochloric acid at temperatures of about 200°); extraction of the hydrochloric acid solution with ether, iron III-chloride (molybdenum, trivalent thallium) being concentrated in the ether-phase, etc., but these have not found much application.

2. Elements of the ammonium hydroxide group or part of them may be separated with other reagents. If not the whole group is precipitated the remainder is ordinarily found by a subsequent treatment with ammonium hydroxide, when necessary after expulsion of the other reagent. Such procedures are in general not well suited when still other determinations (alkaline earths, magnesium) are to be made in the same portion, either as the volume of the solution will be materially increased by an additional precipitation or as it will take considerable time to remove undesirable substances from the liquid.

2a. To co-precipitate *manganese* completely with the ammonium hydroxide precipitate, [35]) add to the slightly ammoniacal, boiling solution 25 ml of saturated bromine water drop by drop, the liquid being kept alkaline by the simultaneous addition of ammonia. Manganese is precipitated as peroxide while nickel and chromium remain in solution, the latter as chromate. Ammonium persulphate and also hydrogen peroxide seem to be unsatisfactory in this respect as in their presence much calcium goes into the precipitate as well as the whole amount of barium present in the sample. An enormous excess of bromine water is required as the following reaction takes most of it:

$$2\ NH_4^+ + 3\ Br_2 \longrightarrow N_2 + 8\ H^+ + 6\ Br^-.$$

The further treatment will be done according to one of the methods described, preferably the titrimetric procedure, otherwise the manganese is most likely to be "lost" again.

2b. Precipitation by phenylhydrazine [36]) after reduction of

iron to the bivalent state (with ammonium bisulphite) serves as a useful separation to determine small amounts of aluminium in presence of much iron, titanium, zirconium, thorium, chromium and in addition phosphorus and vanadium if not present in excess over the precipitated metals. The method is in vogue more or less for commercial analyses of alloys but does not seem to have advantages over the electrolytic methods or the separation with sodium hydroxide solution.

2c. Cupferron [32]) may also serve to yield a preliminary group separation in strongly acid solution. Iron, titanium, zirconium, tin, vanadium, *niobium* and *tantalium* are quantitatively separated from the other elements of the ammonium hydroxide group.

2d. KOLTHOFF, STENGER and MOSKOVITZ [37]) advocate the use of ammonium benzoate for the separation of iron, aluminium and chromium from manganese, calcium, strontium, barium, magnesium etc., in very dilute acetic acid solution).

2e. Freshly prepared solutions of carbonates and oxides of various metals may give a solution of definite pH and are satisfactory for precipitations of metals otherwise separable only with difficulty. In particular separations with oxide suspensions are closely related to the ionic-potential of the elements, cf. fig. 2, p. 3. [38]).

GRAVIMETRIC DETERMINATION OF MANGANESE. GENERAL CONSIDERATIONS.

The gravimetric determination is described here — though scarcely worth while considering in rock analysis — as it changes somewhat the general course. With rocks, a gravimetric determination will seldom be required, or even suitable, as grave errors are easily made in this procedure, due mainly to incomplete separation of the manganese and co-precipitation of other elements. These errors need not necessarily compensate each other and indeed plus errors are more frequent here, than minus ones. The sulphide method is generally used in this case owing to the large amounts of salts present, that will spoil the otherwise very satisfactory nitric acid — chlorate method. Stress may be laid here upon the possibility of determining silica in the portion reserved for the determination of the alkalies [51]) and

treating the main portion with hydrofluoric and nitric acids followed by expulsion of the hydrofluoric acid, conversion of nitrates to chlorides, precipitation of the sesquioxides, elimination of the ammonium salts and applying the nitrate-chlorate method [39]) for the separation of manganese. This is perhaps the most reliable method for silicates containing large amounts of manganese.

Whilst this book was in print, HACKL published a paper on the determination of manganese in silicates [39a]). Manganese is precipitated altogether with ammonia by the addition of a few ml of hydrogen peroxide. (This is not consistent with the statement by HOLT and HARWOOD [39b]) that co-precipitation of calcium is caused by H_2O_2). After re-precipitation in the same way, ignition of the combined oxides and fusion with a mixture of sodium and potassium pyrosulphates, the cake is dissolved in dilute sulphuric acid, care being taken, that the final concentration of the latter is 7 % by volume. Manganese, titanium and iron are determined in this order. Manganese is estimated colorimetrically after oxidation with *potassium* persulphate in presence of silver *sulphate.* (Ammonium salts are partly oxidized to nitric acid and this interferes with the volumetric determination of iron.) Titania is estimated in the same liquid after oxidation with hydrogen peroxide, finally, iron is determined with titrimetric methods. As the presence of iron causes a different colour tone, HACKL advocates the addition of pure ferric sulphate to the standard solution in an amount equivalent to that, present in the test solution. In view of the low percentages of manganese generally found in silicates, the larger errors in the percentages of aluminium — when recorded by difference — should not be risked, to avoid the minute errors in the determination of calcium and magnesium in the standard procedures. On the contrary, for larger percentages of manganese — where the contamination of Ca and Mg by manganese becomes harmful — this procedure is useless.

DETERMINATION OF MANGANESE. PROCEDURE OF SULPHIDE METHOD.

The combined filtrates from the sesquioxide precipitate are evaporated down to about 100 ml and the liquid is meanwhile kept just alkaline by the addition of ammonia when the solu-

tion fails to smell ammoniacal. Ordinarily a slight amount of sesquioxides separates and should be recovered, lest these contaminate the manganese. So, the solution is filtered into a 150 ml Erlemeyer flask; the filter is thoroughly washed with hot water containing 2 % of ammonium chloride, ignited in a small platinum crucible and the weight added to that of the ammonia precipitate. It is advisible to determine the manganese content colorimetrically after fusing the small precipitate with 1 g of potassium pyrosulphate.

The vessel, in which the filtrate of the ammonia precipitate has been evaporated, may contain some manganese dioxide and is therefore rinsed with a few drops of concentrated hydrochloric acid. These washings are added to the filtrate in the Erlemeyer flask. The contents are now made strongly alkaline with ammonia and a current of hydrogen sulphide is passed through the liquid. The flask is provided with a stopper and allowed to stand overnight or 24 hours. After this time the sulphides of manganese and other bivalent metals are filtered off. The filter is washed with a solution containing both ammonium chloride and ammonium sulphide, made by passing a stream of hydrogen sulphide through dilute ammonia, 1 : 5, already partly neutralised with hydrochloric acid and finally making the liquid distinctly alkaline. The filtrate is reserved for the determination of lime and magnesium and need not be freed from sulphide for this purpose.

The sulphides on the filter are next washed with hydrochloric acid, 1 : 5, saturated with hydrogen sulphide (The black precipitate which remains on the filter after this extraction may contain the metals nickel, cobalt and copper in the form of their sulphides, together with some platinum, derived from the vessels. It is inadvisible to determine any of these metals here, as they are likely to have been introduced in the course of the analysis.) This treatment will bring the sulphides of manganese and zinc into solution. If zinc is absent, and even when this metal is present in negligible amounts, the manganese is precipitated in the same manner as magnesium in the form of the double phosphate with ammonium and ignited to be weighed as pyrophosphate. Factor for MnO : 0.49975 (0.5)
Mn : 0.38704

In case that much zinc is present, the liquid is evaporated down, taken up in a few drops of sodium carbonate solution,

again evaporated to dryness to destroy the ammonium salts, dissolved in a few drops of diluted hydrochloric acid and manganese is precipitated as carbonate by the addition of sodium carbonate solution. The precipitate is filtered off on a small filter and converted into pyrophosphate as has been described above.

As an alternative the sulphide may be converted into sulphate; this is far more accurate than weighing it in the form of the oxide as this has an indefinite composition (approx. Mn_3O_4).

The slimy sulphide precipitate is more conveniently filtered when after complete separation of the sulphide, a solution of 0.4 g $HgCl_2$ in 10 ml water is added at one pouring whilst vigorously stirring. [40]) For larger amounts of manganese and zinc (up to 200 mg) only 0.05—0.1 g mercuric chloride is required. The mercury compounds are removed by heating *under a powerful hood.* The contents of the crucible, in which this operation is carried out, may be treated with a slight excess of concentrated sulphuric acid and the metal is determined as manganese II-sulphate. This salt should not be heated at a temperature higher than 400°. Factor for MnO 0.46983
for Mn 0.36387

It is difficult to expel the excess of sulphuric acid; therefore the ignited precipitate is dissolved in a few ml of water, again evaporated and heated to constant weight.

DETERMINATION OF CALCIUM AND STRONTIUM. GENERAL CONSIDERATIONS.

After the separation of the sesquioxides — if necessary also of manganese —, the alkaline earths, magnesium and the alkali metals remain in solution, with a large amount of ammonium salts. The latter are harmless, even beneficious in the precipitation of calcium — by preventing the co-precipitation of magnesium — strontium, however, is kept more or less in solution, but this will not exceed one tenth of the total amount of strontia under the conditions of silicate rock analysis even with double precipitations; so this error may be neglected. The solution is obviously useless for the determination of the alkalies, owing to the large amounts of salts of these metals, introduced subsequently. Magnesium is usually separated as double phosphate

with ammonium; only if the separation of much calcium from small amounts of magnesium is called for, the 8-hydroxyquinoline-method offers special advantages. This case though being rather rare in silicate rock analysis, is dealt with in the section on magnesium; it will be encountered frequently in the analysis of magnesite deposits.

Calcium and over 90 % of the strontium are separated as oxalate. Double precipitations are required, to make the separation from magnesium and sodium complete. If manganese is still present in the solution, a correction may be applied for the very slight contamination of the precipitate by this metal, generally this amount is negligible.

The oxalate may be weighed (after GOY [41]) or ignited to carbonate (in a filter crucible) or to oxide. The three methods yield equally satisfactory results. The titration method will not be given here, as it prevents the application of a correction for manganese, as well as the determination of strontium. Barium, if occurring in amounts warranting its determination, should be separated as sulphate before proceeding with the analysis of magnesium. The exact determination of this constituent, however may better be done in a separate portion of the sample.

DETERMINATION OF CALCIUM AND STRONTIUM. ANALYTICAL PROCEDURE.

In cold solutions the separation of calcium oxalate is slow and the precipitate so fine-grained as to go through the filter. In boiling solutions, the precipitate becomes coarsely crystalline but objectionable amounts of sodium and magnesium are precipitated. The most favourable temperature will be 80°. Concerning the other conditions, it may be remarked, that although the solution may be distinctly ammoniacal, an acetic acid-ammonium acetate buffering solution will perhaps serve still better less magnesium being co-precipitated. In either case, add to the hot liquid under constant stirring, at first drop by drop and when the precipitate has formed, gradually, one fourth part by volume of a freshly prepared ammonium oxalate solution — saturated at 20°. The p_H should be kept within the limits 5—9 After all has been added, keep on a water bath for one hour, then add a few ml of ammonia, until a distinct, but by no means dis

agreeable ammoniacal odour results and allow to cool with occasional stirring. Filter four hours after cooling has started and wash with a cold 0.5 % ammonium oxalate solution two or three times.

At first the addition of the precipitant should be drop by drop to secure the formation of a relatively small number of crystallization centres. This and keeping the liquid warm for some time, promotes the formation of a coarsely crystalline precipitate; the addition of ammonia, after precipitation is complete, makes the precipitate less soluble in the liquid.

Dissolve the precipitate in dilute hydrochloric acid, now taking a much smaller beaker (250 ml). The volume should not be less than corresponds to 1 mg CaO/ml. Re-precipitate in this solution now being almost free from interfering elements. Therefore add a few ml of ammonium oxalate solution, heat to 80° and neutralize the liquid by adding diluted ammonia drop by drop, until the precipitate has been completely formed. The further treatment of the precipitate should be carried out as described above; filter and wash with 10 ml of the cold washing solution four times. In these filtrations, care should be exercised to prevent the over-filling of the filter as the still rather fine precipitate then has a strong tendency to "creep" along the walls of the funnel. If a paper filter is used this should be as small as possible. The united filtrates are reserved for the determination of magnesium.

The calcium may be determined as oxalate [41]), provided a filter crucible has been used — not a paper — and other organic matter, especially paper fibres, are absent. In *this* case the washing should be repeated once with 10 ml of a 0.1 % cold ammonium oxalate solution and finished with twenty *drops* of slightly ammoniacal water. The crucible with contents is dried for one hour at 100—105°; higher temperatures should be avoided. The precipitate answers to the formula CaC_2O_4. 1aq.
Factor for CaO : 0.38389.
for Ca : 0.27437.

In the porcelain filter crucible it is easily converted into carbonate at temperatures not exceeding 600°; 250° is already quite sufficient. If, however, a paper filter has been taken, this should be incinerated previous to the final ignition and the latter is best carried out in a Rose crucible, carbon dioxide being introduced to convert any quick lime possibly formed in the paper

ash. An ordinary crucible and a few pieces of ammonium carbonate may serve as well for this purpose. The use of a filter crucible, however offers many advantages.

Factor for CaO : 0.56037.
for Ca : 0.40049.

The ignition to oxide should be carried out in a platinum crucible, a few minutes heating at 1200° over the blast being sufficient. Quite satisfactory results can be obtained with a large Meker burner. Too prolonged heating should be avoided as the crucible is likely to be attacked more or less. Conversion of the oxide into sulphate or fluoride is not recommended as this would prevent the estimation of strontium and manganese in the precipitate. There is little preference as to the other three described forms of weighing.

DETERMINATION OF STRONTIUM. PROCEDURE.

The various methods proposed for the determination of strontium in calcium oxalate precipitates and the conditions effecting the complete separation of these elements are clearly discussed by NOLL [42]). So, only the very satisfactory procedure of RAWSON [43]), re-investigated by NOLL, will be given here. Either carbonate or slaked oxide is transferred into a small pyrex beaker, converted without loss into nitrate and the latter is dried at 160°. By mixing concentrated nitric acid (d = 1.40) with the red, fuming acid (d = 1.54), an acid is prepared with specific gravity about 1.45 (not less than 1.44, not more than 1.46). For every mg of CaO, 0.3 ml of this mixture will be used altogether. One fifth part of the required amount of acid is digerated with the salts; the solid remnant is transferred to a porcelain filter crucible and repeatedly washed with the rest of the acid in as small portions as is practicable. The strontium is weighed as nitrate after drying at 160°. or may be converted into sulphate.

Factors: Sr-nitrate; for SrO : 0.48972.
Sr-sulphate; for SrO : 0.56419.

Small amounts of manganese will not interfere here and may be estimated in the filtrate by colorimetric methods. The strontium, not caught in the calcium oxalate may be recovered by adding an amount of strontium- and magnesium-free calcium salt to the filtrate from the original oxalate precipitates, followed

by recovery of the strontium, as has been described above, or a correction of + 10 % may be applied. In most cases this will be an unnecessary refinement. Other methods for the separation of strontium and calcium, satisfactory for larger amounts of strontium, will be given in the chapter on mineral analysis. The percentage of lime is to be corrected for its strontium content.

DETERMINATION OF MAGNESIUM. GENERAL CONSIDERATIONS.

Barium and manganese interfere in the determination of magnesium as pyrophosphate. Barium can be removed as sulphate p. 162) and this should be done if large quantities are present, as the composition of the ignited barium phosphate is indefinite and a correction, therefore, cannot be applied. The largest part of the manganese present in the sample will be weighed as pyrophosphate together with the magnesium pyrophosphate. Hence this metal should be determined colorimetrically in the nitric acid solution of the combined salts. Excessive quantities of ammonium compounds and oxalates prevent the complete and rapid precipitation of magnesium ammonium phosphate and should consequently be avoided as much as possible. Destroying the ammonium salts, however, will rarely be necessary, except when very little magnesium is present. Further, it has not proved feasable to obtain a precipitate of definite composition in but one precipitation; this can only be attained if nearly equivalent amounts of magnesium and phosphate are together in a solution, free from interfering metals, especially alkalies. All these difficulties are largely overcome by making double precipitations: in the first operation, the favourable conditions for the final treatment are secured. It is obvious that the percentage of magnesium here found will be correct only, if the former separations have been carried out in a correct way, so as to prevent the co-precipitation of magnesia with the sesquioxides and with the lime. Therefore double precipitations for these groups are obligatory and in the case that very much magnesium is present (only met in "basic" rocks), triple precipitations may be required [44].

There is an excessive abundant literature on this subject. As clearly shown by the recent work of Miss Epperson, there is not much preference to any of the different methods, provided double precipitations are made, the phosphate is added to the

acid solution and larger quantities of sulphate and citrate are absent [44a].

The 8-hydroxyquinoline method presents some difficulties if either large amounts of liquid are to be treated, or much oxalate is present. Consequently it seems better to carry out a separation of magnesium by means of this very valuable reagent prior to the determination of the alkaline earths. [45]

DETERMINATION OF MAGNESIUM. PROCEDURE.

After the separation of calcium — if necessary also of barium — the liquid is acidified slightly with hydrochloric acid, concentrated in a fused silica or new porcelain dish as far as will be possible without the formation of solid salts and transferred to a beaker of suitable size, preferably new and on no account with scratches on the inside walls. A freshly prepared, filtered solution of any soluble phosphate (e.g. disodium-, microcosmic- or better diammonium phosphate) is added in 5-10 fold excess or even more for very small quantities of magnesium and in addition to these amounts, 1 g of the salt in concentrated solution may be added for every 100 ml of liquid in the vessel. Then, concentrated ammonia is added drop by drop under constant stirring, until a precipitate is formed or a decided ammoniacal odour persists even after thorough stirring. In the former case the further addition of ammonia is delayed a few minutes whilst stirring, so that the precipitate may become crystalline. Then, drop by drop, more ammonia is added until no more precipitate is formed. A few drops of phenolphthaleine solution are given in either case and more ammonia is added gradually until a faint red colour is imparted to the liquid and the beaker is placed for some hours on the water-bath, the contents being occasionally stirred. The stirring rod should be furnished with a small piece of soft rubber tubing to avoid even very slight scratching of the vessel, as this causes the separation of tenaciously adhering crystals of the precipitate on the walls. The rod is washed with a few drops of water after using and placed in a suitable stand; do not leave in the liquid. After cooling, about 50 ml of concentrated ammonia are added — this has the purpose of making the precipitate less soluble — and the beaker is set apart for at least 24 hours (preferably during a weekend). After this time the solution is filtered and the beaker and filter are washed three

times with adequate portions of dilute (5 %) ammonia. The crystals on the filter are rinsed with water into a small beaker (250 or 400 ml, according to the mass of the precipitate) whilst the parts of the precipitate that adhere to the walls of the previously used beaker are dissolved in dilute hydrochloric acid, 1 : 4. The resulting liquid is quantitatively transferred to the beaker with the main mass of the precipitate and the filter is likewise washed thoroughly with the acid. The liquid in the small beaker now contains all the magnesia of the rock with about the required amount of phosphorus salts and the volume should be about 100 ml for 0.1 g. MgO. To be safe, a few crystals (0.25 g) of diammonium hydrogen phosphate are added to yield a slight excess and the second precipitation is carried out in exactly the same way as the first one. The final filtration, however, can be done here a few hours after the liquid has reached room-temperature, owing to the favourable conditions that will now exist (greater concentration, absence of large quantities of ammonium salts, etc.) The precipitate is well but not over-washed, again with 5 % cold ammonia and the walls of the beaker may be cleansed, either with the aid of a piece of filter paper, or with the rubber-covered glass-rod. Filtration may be effected in a filter crucible or on a paper filter. In both cases the ignition should be carried out very cautiously in the beginning of this operation, as the expelled NH_3 might exercise a reducing action on the rest of the salt, this being detrimental to the platinum crucible, besides causing low values. The paper should likewise and for the same reason be charred and burnt very caferully. There are no serious objections to the use of a platinum crucible by an experienced chemist. To be safe, a fused silica crucible may be taken and will render excellent services; it is more difficult to obtain a perfectly white pyrophosphate in silica or in porcelain, than in platinum. Nitric acid, however, should never be used to obtain a pure white salt as losses are likely to arise through this practice. To prevent reduction of the pyrophosphate, the flame should not be allowed to envelope the whole crucible and only the oxidizing upper part of the flame is to be used; a Meker burner therefore may be advisible. A blast is generally not necessary, but may be applied to volatilize an excess of P_2O_5 that now and then occurs; constant weight cannot be reached with a blast and the heating at these high temperatures should not last more than 5—10'. The most con-

venient method for the ignition, however, is in a filter crucible in an electric furnace. In this case the heat should also be applied gradually and the temperature must not exceed 1000°. The precipitate is not hygroscopic and may be weighed after one hours cooling of the crucible in a dessicator or in the balance case. After constant weight has been reached, the mass in the crucible is transferred quantitatively to an Erlemeyer flask, diluted nitric acid, 1 : 4, is added and in the resulting liquid the manganese is determined colorimetrically. The amount of MnO found, is multiplied with the factor 2 (properly: 2.0010). This, subtracted from the weight of the combined precipitate yields the magnesium pyrophosphate. Factor for MgO : 0.36214.
for Mg : 0.21846.

The filtrates from the magnesium pyrophosphate may be rejected if after a few days standing no further precipitate or at most a mere trace is formed. Otherwise this precipitate should be recovered and treated in the same way as the rest of the phosphate.

8-HYDROXYQUINOLINE-METHOD FOR THE DETERMINATION OF MAGNESIUM.

This organic reagent is suitable for separating magnesium from the alkaline-earthmetals as well as from the alkalies. [45]) As only volatile material is introduced, this method may serve in the case that, owing to lack of sufficient amount of material, the alkalies are to be determined in the main portion, either after decomposition by acids, or by fluxes which can be removed (p. 41; boric oxide, lead oxide). For low amounts of magnesium, to be separated from large quantities of alkaline earths, this method is equally valuable. The order of determination had better be changed in this event; so, after the separation of the sesquioxides — and possibly manganese as sulphide — magnesium may first be precipitated in a solution containing 5—10 g of ammonium acetate. The addition of 10—20 ml twice normal sodium hydroxide solution and 4 g of tartaric acid yields such conditions as make possible the direct separation of magnesium from heavy metals. Aluminium, cadmium, copper and zinc — if present in the solution — should be previously separated by means of oxine in acetic acid solution, but in the case of rock analysis these precautions are unnecessary.

The contents of the beaker are heated to 60—70° and a concentrated solution of 5—10 g ammonium acetate is added, followed by a slight excess of "oxine"-solution. Then, the liquid is made decidedly ammoniacal; this causes the precipitation of magnesia. The precipitate is allowed to settle somewhat and the liquid is then decanted through a filter. A yellow colour of the solution indicates that enough oxine has been used, the excess should be small. If alkaline earths or other metals besides alkalies are present a re-precipitation is required. The precipitate is dissolved in a slight excess of hydrochloric acid and after addition of 1—2 g ammonium acetate and a few drops of the oxine solution, the liquid is made just alkaline with ammonia, boiled 2—3' to obtain a crystalline precipitate and the latter is filtered off on a rather coarse sintered glass filtering crucible. Thorough washing with hot dilute ammonia (2 %) is required to free the precipitate from excess oxine. The precipitate can be dried at 100—105°, 130—140°, or may be ignited to constant weight — to the oxide — without the addition of oxalic acid as has been recommended [46]). As an alternative, the precipitate may be dissolved in hydrochloric acid and estimated volumetrically with potassium bromate solution.

When dried at 100—105° the composition of the precipitate is: $Mg(C_9H_6ON)_2, 2H_2O$, factor for MgO : 0.11574; for Mg : 0.06982

When dried at 130—140° the composition of the precipitate is: $Mg(C_9H_6ON)_2$, factor for MgO : 0.12908; for Mg : 0.07786.

Manganese accompanies magnesium in the precipitate; a correction can be applied after destruction of the organic matter. Small amounts of oxine will not interfere with the determination of calcium and strontium as oxalates. According to the scheme employed, the alkaline earths, including barium may be determined in the filtrate and the alkalies also, provided that no alkali salts are introduced throughout the whole analysis and it is considered that contamination by alkalies derived from the vessels is negligible, though this will seldom be the case. Otherwise the liquid is to be rejected.

DETERMINATION OF THE ALKALIES. GENERAL CONSIDERATIONS.

In silicate rocks, of the alkalies, sodium, potassium and lithium are nearly always present, the latter element, however, only in

mere traces; these can be detected by means of a spectroscope. The analysis of lithium minerals will be treated later on. Methods for the detection of rubidium and cesium will not be given in this book, as these metals are both unimportant and to a high degree uninteresting to the analyst. Spectrographic methods are appropriate here.

The LAWRENCE SMITH method [47]) for the determination of the alkalies will be described here in great detail whilst BERZELIUS' procedure will be briefly mentioned. [48]) Even in the case of acid soluble materials, this procedure has many advantages over the wet attack, as the separation of most other elements is effected by the very decomposition of the material. There are two objections to the method. First, SMITH has advocated the use of a special designed platinum crucible, the so-called finger crucible. This form, though having many advantages, is expensive and can only be used in this determination, but WASHINGTON showed that equally accurate results may be obtained with a platinum crucible of the usual form, provided proper care is exercised during the ignition. [49]) The second one is the necessity of a sufficient pure, alkali-free calcium carbonate for the attack. This can be rarely obtained from dealers, but the preparation in the laboratory of a stock, large enough for several hundred decompositions is rather easy. In this stock, the alkali-content is determined once and for all and if not too large, a correction may be safely applied.

The fusion and further operations yield the alkalies as chlorides, the most convenient form for their separation. One of the metals is subsequently separated and the other determined by difference. If larger amounts of lithium are present, this constituent should also be determined or estimated separately. Only if extreme economy with the sample is imperative, should the methods of wet attack in the case of acid soluble minerals, or else fusion with boric- or lead-oxides be applied. It seems, however, to be more reliable, to carry out the same operations as to be described here, on smaller samples. With rock samples this will rarely be necessary.

For the separation of sodium and potassium a choice may be made between a number of different or variant methods; some of these will be described here in full and the others mentioned briefly.

DETERMINATION OF THE ALKALIES. PROCEDURE.

A specially prepared, extremely fine portion of the sample is required for this attack, as complete fusion does not take place and, on the contrary, should be avoided. The fine powder is thoroughly mixed with calcium chloride and oxide. In the method as described by SMITH this is attained by mixing the rock powder with ammonium chloride and calcium carbonate. Gentle warming causes the formation of calcium chloride by double decomposition and further heating yields quicklime by dissociation of the carbonate. It is rather difficult, however, to secure a homogeneous mixture by applying this procedure and the operation requires much skill and considerable time. My experience is, that the first part of the analysis becomes simpler when performed as follows.

About 0.5 g (0.49—0.51) of the pure calcium carbonate is weighed out, placed in a very clean agate mortar and covered with a small inverted funnel. Concentrated alkali-free hydrochloric acid is introduced through the stem drop by drop, until only minute amounts of carbonate remain undecomposed. Next, about 0.5 g (0.4—0.6) of the sample, exactly weighed, is added to the liquid in the mortar and with the clean pestle, the sample is ground rather fine. As mechanical losses need not be feared, this may be done in a few minutes. If the sample contains much biotite, the grinding should be very careful, as according to JAKOB this mica tenaciously resists attack. [50]) Then, gradually, most of a portion of about 5 g pure calcium carbonate (weighed to one tenth of a gram), is added, the mass being kept of a pasty consistency by the simultaneous addition of a few drops of alcohol, preferably methyl alcohol. This considerably facilitates arriving at a uniform mixture by eliminating the tendency of the dry calcium carbonate to "cake". The finer the powder, the greater will be this tendency and the calcium carbonate as prepared in small portions in the laboratory *is* extremely fine. In the case of a dark sample, the homogeneity of the mixture can be judged by the colour. With light-coloured, or even white, samples the mixing should be duly prolonged to be safe in this respect. When the mixing is considered to be complete, a stream of clean warm air is directed on the contents of the mortar and soon these will be dry enough to be transferred to the crucible without loss. A finger crucible should be used or

if this type is not available, a normal *high* model may be taken.

The finger crucible may be of porcelain, nickel or sheet iron, although a platinum one is better. When silica is to be checked after the extraction of the alkalies, a porcelain crucible should not be used as the porcelain is slightly attacked by the flux. In checking the iron content of the sample it is evident, that the use of a crucible made of this material is out of the question.

In either case, the bottom is covered with a thin layer of carbonate of the same 5 g-portion, the contents of the mortar are transferred to the crucible with proper care to prevent contamination of the upper parts of the walls, the mortar, pestle and the platinum spatula used in this operation are twice dry-washed with the rest of the calcium carbonate and the "washings" are added to the contents of the crucible. As the volume occupied by the fine calcium carbonate may be considerable, when dry, the pasty state of the mixture is a decided advantage here, as it greatly diminishes this volume. Another improvement in this procedure is, that the fine grinding of a weighed portion can be made without loss, so preventing the necessity of weighing out the portion *after* grinding it. The latter practice is objectionable, because the composition of the sample is affected by the operations; ferrous iron is likely to be oxidized and the amount of water may rise considerably, both alterations will decrease the apparent alkali-content.

The mass is dried completely in the uncovered crucible over a low flame or better in an oven. When the contents of the crucible are wholely dry, the "fusion" is carried out at a bright red heat for about one hour. If a finger crucible is used, it is inserted in an exactly fitting hole bored at a downward angle in a fireclay cylinder. A piece of asbestos board at a distance of a few mm from the cylinder wall serves still more to provent the upper part of the crucible becoming too hot. If an ordinary crucible is used, this should be placed in a hole in a thick horizontal asbestos shield. Only the lower third of the crucible should be under the shield and in both cases, the contents shoulds not take more room, than may be safely heated at as high temperatures as are required without fear of loss of the volatile alkalies. An ordinary crucible should have a well-fitting lid and a platinum basin filled with water on the latter. [49]) If now and then fresh water is added, boiling need not be feared and the temperature in the upper half of the crucible will be low enough.

After the full heat has been applied for 45—60', the crucible is allowed to cool; the core will be found to be more or less loose from the wall in a sintered state and is transferred to a fused silica dish. In this the quick lime is slaked first with a *few* drops of water. If the mass in the crucible is partially fused and does not separate readily from the walls it should be soaked *in* the crucible with enough water to cover the contents; this may be prevented by taking enough carbonate. *Therefore, in the case of "basic" rocks 6 g of calcium carbonate may be weighed out for this fusion.* The complete disintegration is advantageously shortened by placing the dish on the slowly boiling water-bath. The crucible, filled with water is also placed in a hole on the water bath; a finger crucible should be inserted into a small Erlemeyer flask, filled partly with water and heated over a low flame.

The cake will ordinarily decompose readily within half an hour, small solid lumps may be broken up with an agate pestle or nickel spatula. The solution in the crucible is added to the basin and the supernatant liquid is decanted through a 9 cm filter into a beaker of 400 ml capacity. The latter should be reserved exclusively for the alkali-determinations and though one of fused silica is preferable, a resistance glass of low alkali content will also suffice. The crucible is again filled with water, emptied into the basin and after a few rinsings crucible *and lid* will be free from alkalies. Small portions of alkali-free water are repeatedly added to the mass in the crucible and then decanted through the filter. With 150—200 ml of water altogether, the alkalies may be supposed to have gone quantitatively into the filtrate. The water used in this determination should be caught direct from the still in a flask that cannot possibly give off alkalies, e.g.one of silver, bakelite or ceresine.

The decomposed mass may still serve for several purposes, in the first place, to determine whether the attack has been complete. This can be easily combined with a check for silica and iron in the following way. [51]) The resulting mass is treated with a mixture of 60 % perchloric acid containing 7 % hydrochloric acid of spec.gr. 1.10. The powder should disappear altogether, without leaving gritty particles, perhaps but a few grains of ore; these will dissolve only very slowly. Particular care should be taken with regard to undecomposed flakes of mica, these should not be present. [50]) If either of these conditions is not ful-

filled, the whole operation had better be repeated. The liquid is heated on an sandbath until heavy white vapours of perchloric acid are evolved. After cooling, the mass is digerated twice with 70—80 ml of 10 % hydrochloric acid and is then filtered, washed with hot dilute hydrochloric acid, followed by water and the silica is treated and weighed as has been described in a former section, p. 44—46. Several authors claim that the impurities are negligible in silica thus prepared.[51)] [52)] In the filtrate from silica, total iron can be determined by titration according to the ZIMMERMANN-REINHARDT method. This method is described in manuals on volumetric analysis.[53)]

If the decomposition has been complete, very little alkalies are retained in the decomposed mass from the fusion cake, consequently, repeating the fusion with this mass, after the extraction of the alkalies and after some calcium chloride or sal-ammoniac has been added, is considered to be wholely superfluous. Indeed the adsorbed alkalies are nearly corrected by the blank determinations, whilst a complete decomposition is easily obtained, if the conditions described are adhered to.

Calcium is removed from the filtrate by means of ammonium carbonate. A cold saturated solution of this salt is gradually added to the slightly ammoniacal *boiling* solution in the beaker. When no more precipitate is formed, further addition of the precipitant will only cause considerable spluttering owing to the dissociation of the salt. For the same reason it is impossible to prepare the carbonate solution by *heating* water together with the salt. The calcium carbonate is filtered off, the filtrate being caught in the clean silica dish. After duly washing the filter and precipitate with dilute ammonia (2 %), the dish. containing the alkalies from the sample as chlorides besides appreciable amounts of ammonium salts and perhaps still traces of calcium, magnesium and sulphate ions, is placed on the water bath and the contents evaporated to dryness. The dish is then covered with a filter paper and placed in the oven at 130°. The purpose is, to dry the salts thoroughly to prevent decrepitation in the subsequent heating. After 30—60' the dish is placed on a ring on a stand in the hood, covered with a clock glass and a *low* flame is waved below the entire surface of the dish. If any decrepitation is observed, the heating is stopped instantly and the dish is placed — covered with paper — in the oven for another hour. Ordinarily, however, all will go well, the clock-

glass may be removed, the flame is raised gently and given a waving motion so as to reach any part of the surface of the dish in every 5". Thick vapours of ammonium salts are liberated. The sublimation should not be hastened as this may cause mechanical loss of alkalies with the ammonium salts. When the development of ammonium salt vapours ceases, the dish is allowed to cool while covered with the filter paper. A small funnel is prepared with a filter of 5 cm diameter and a platinum crucible placed below to catch the filtrate. The salts in the dish — coloured by carbon particles derived from the ammonium carbonate — are dissolved in a few drops of water. If much sulphide or sulphate was present in the sample, a considerable part of it goes as sulphate radicle through the various operations into the final solution. It is best removed direct before the filtration into the crucible, by treating the concentrated solution with a few drops of barium chloride solution, filtering and removing the excess of barium together with traces of calcium, which may still be present here, as oxalate. The volume of the liquid will have increased in these operations and must therefore be reduced again. The liquid is evaporated down in the crucible, and heated as will be described, followed by convertion of the alkali carbonates which may be formed as a result of this procedure, by adding a few drops of concentrated hydrochloric acid to the diluted solution of the salts in the crucible. Generally this will not be needed, obviously not, when the alkalies are weighed in the form of their sulphates. Likewise proper care should also be taken to prevent excessive contamination by flame gases.

To the few drops of water, used to dissolve the salts in the dish, one or two drops of the ammonium carbonate solution are generally added and these should give no visible precipitate this time, otherwise the precipitation with ammonium carbonate may have to be repeated as described above. Very cautiously and with the aid of a thin glass rod, the liquid is run onto the filter and, with only a few drops of water at a time, the alkali salts are quantitatively washed into the crucible. The latter should not be more than half filled. After that, the liquid is evaporated on the waterbath or at an appropriate height over an electric hot plate.

When dry, the contents are moistened with a drop of hydrochloric acid to convert any carbonate into chloride. The last

traces of ammonium salts should now be removed carefully. Therefore, when the contents are again dry, the crucible is placed for 30' in the oven (130°). After this time, the crucible is placed on a support in a stand and is covered with a resistance glass watch-glass of about the same size as the lid. With a very low flame (height about 2.5 cm) waving under the crucible, the temperature is gradually raised until a sublimate of sal-ammoniac on the cover prevents further inspection of the inside of the crucible. Crucible and cover are allowed to cool completely and then the watch-glass is cleaned by gently heating it over the flame, the latter being carefully inspected for any trace of colour, indicating escape of sodium or potassium. In this way the salts are heated until no further sublimation takes place and until the salts are only just fused, the flame being immediately withdrawn when this is observed. When the crucible is cool, its own lid is quickly substituted for the watch-glass and the crucible weighed directly after it has taken the temperature of the balance. *Sodium chloride which has been fused is slightly hygroscopic.* The gain in weight is reported as NaCl + KCl, though in very exact work two minor corrections may have to be applied (NaCl + KCl + x + y). The alkalies may be weighed also as the less volatile sulphates, — but this will make their separation more troublesome — by evaporating down the salts with an excess of dilute sulphuric acid, followed by carefully expelling this excess by volatilization, a small piece of ammonium carbonate being introduced twice into the hot crucible, to ensure the decomposition of pyrosulphates. Again, the chlorides may be converted into carbonates by evaporating them down in solution with excess of oxalic acid, followed by gentle heating.[54]) The carbonates may be titrimetrically determined with standardised hydrochloric acid and the chlorides thus formed may serve for the separation of the two metals. By a treatment of the sulphates or chlorides, with hydroiodic acid (H I) iodides are obtained.[55]) If, however, the method described is carried out with proper care — and the watch-glass has been used — no loss of alkalies need be feared at all and the more intricate procedures are therefore not recommended.

SEPARATION OF THE ALKALIES. GENERAL CONSIDERATIONS.

The alkalies are now to be separated and if one of them has been determined, the other may be found safely by difference.

Various procedures have been described. In most of these, potassium is first separated, either as chloroplatinate [56] or in the form of the perchlorate [57], both salts being insoluble, especially in alcoholic media. The separation of sodium as triple acetate of uranyl, magnesium or zinc and sodium [58] has found comparatively little application but is perhaps the most accurate method when only sodium is of interest and potassium is present in large excess. The extraction with mixtures of organic solvents such as normal and iso-butyl alcohol, amyl alcohol, ethyl acetate, ether, pyridine etc., is especially suitable when lithium is also to be determined [59] The sodium cobaltinitrite method will not be described, as only a separation is obtained and potassium has still to be determined subsequently by one of the other methods.

THE SEPARATION OF SODIUM AND POTASSIUM. PROCEDURE.

1. THE CHLOROPLATINATE METHOD.

This method renders excellent service, and the cost need not be high when the platinum is recovered. Both alkali chlorides are to be converted to chloroplatinates, as sodium chloroplatinate is easily soluble in the washing-solution, in contrast with sodium cloride. In this version of the method, sulphates should be absent and in any case the operations should be carried out in an atmosphere as free from ammoniacal vapours as possible, as the free chloroplatinic acid easily combines with gaseous NH_3, yielding the insoluble ammonium compound. The potassium salt is almost insoluble in 80 % alcohol (ARCHIBALD 1 : 10.000; PRECHT 1 : 26.400 [60]); usually negligible; alcohol saturated with potassium chloroplatinate cannot be kept for a long time as aldehyde is formed; this increases the solubility).

The salts in the crucible are quantitatively rinsed into a small porcelain or fused silica dish (5—6 cm), to be reserved for this work. Any insoluble residue should be filtered off and weighed, this represents the correction "x" in the combined chlorides (ordinarily a few tenths of a mg). Enough of a chloroplatinic acid solution containing 10 % platinum metal is added, to convert the potassium and sodium chlorides to chloroplatinates.

The necessary calculation is made on the assumption that the chlorides consist only of sodium salt. Every 0.1 g of NaCl requires 1.68 ml of the above solution. For the amount of KCl present, this will be an excess of about 20 %. The liquid is evaporated on the water-bath. The precipitated potassium salt should at first dissolve entirely, lest some liquid be occluded and if such be the case, a few ml of water are added. The mass must not be allowed to become completely dry; a syrupy consistency indicates, that when cool, the salts will solidify. The cold mass is soaked with alcohol of specific gravity 0.86 (5 vol. of 96 % alcohol with 1 vol. of distilled water) and the crystals are crushed and broken up with a small glass rod. The liquid is decanted through a small filter (5 cm in diameter), the heavy precipitate being kept as much as possible in the dish. The salt should be washed repeatedly with alcohol of the above concentration until the washings are colourless and the filter clean. If sodium or lithium is to be determined directly, the filtrates are to be reserved. If the first liquid is not at all yellow, not enough chloroplatinic acid has been added and white crystals of sodium chloride will likely be present. In this case the evaporation — now with an excess of the acid — should be repeated. Finally the crystals should be golden yellow. Orange specks show the presence of sodium chloroplatinate and further washings are required in this case. The mass in the dish and the filter are allowed to dry, as alcohol would exercise a reducing action in the subsequent heating. The small amount of potassium chloroplatinate on the filter is dissolved in hot water and added to the contents of the dish. The solution is evaporated to dryness and the *covered* dish is placed for one hour in the oven at 130—135°. Decrepitation is likely to occur at first. When dry and cool, the precipitate is weighed as K_2PtCl_6. Apply the correction for the alkali-content of the reagents.

Factor for KCl : 0.307 (0.30661).
K_2O : 0.194 (0.19374).

The use of the very "accurate" or even of empirical factors — often given to as much as 6 decimals — is entirely superfluous here. The calculated amount of KCl is subtracted from the combined chlorides. Na_2O is found by multiplying the amount of NaCl with the factor : 0.530 (0.53032).

Sodium may be checked by direct determination in the filtrate by the following procedure: The filtrate is heated, until

most of the alcohol is evaporated and it is then treated at the temperature of the water-bath with a stream of pure hydrogen. When the reduction is complete, the suspension is filtered, filtrate and washings are caught in a platinum crucible with tightly fitting lid. The solution should be evaporated in the crucible, in small portions at a time and sodium is determined in exactly the same way as the combined chlorides were formerly. Factor for Na_2O as above. A small particle of the salt may be tested spectroscopically for lithium. In the rest or — if sodium has not been determined directly — in the reduced filtrate from the potassium chloroplatinate, a trace of magnesium can be ordinarily determined as magnesium ammonium phosphate and the correction "y" on p. 79 for Mg_2OCl_2 can be applied. Sodium can be determined also as the sulphate; a minus error due to volatilization as well as plus errors due to hygroscopicity need be less feared then. Another procedure which can be applied even in the presence of magnesium, calcium, barium, ammonium and considerable amounts of potassium, the determination of sodium as triple acetate, will be described in the chapter on plant-ash. Na_2SiF_6 is obtained when the chloride or nitrate is treated in a platinum dish with thrice the stoichiometric amount of SiO_2 and 1—2 ml 40 % HF for every 0.1 g silica, followed by drying at 120° and weighing of the non-hygroscopic salt in the open dish. [61]) A titrimetric method for this determination is also very convenient: $Na_2SiF_6 + 3\ CaCl_2 + 3\ H_2O = 3\ CaF_2 + H_2SiO_3 + 4\ HCl + 2NaCl$.

With Na_2SiF_6 the factor for Na_2O is : 0.32964.

2. MODIFIED CHLOROPLATINATE METHOD FOR SULPHATES.

If the combined alkalies have been weighed as sulphates, the evaporation with chloroplatinic acid will yield the insoluble potassium salt, sodium sulphate, however, remains unchanged. The following artifice, due to LINDO and worked out by GLADDING will be useful here. [62]) After the solid salts have been washed with enough 80 % alcohol, they are decanted with small portions at a time of the following solution: 100 g ammonium chloride are dissolved in 500 ml water; 5—10 g pure potassium chloroplatinate are added. After frequent shaking and standing overnight, the liquid is filtered and will be ready for use *at the*

same temperature. If no white grains are left, the washing is repeated once or twice with 80 % alcohol.

Another possibility is, to reduce the mixture of K_2PtCl_6 and Na_2SO_4 as has been described for the sodium salt, or with metallic mercury in platinum vessels, or with magnesium ribbon in hydrochloric acid solution, followed by ignition and weighing of the filtered platinum. Factor for KCl : 0.76331.

K_2O : 0.48232.

3. SEPARATION WITH THE PERCHLORATE METHOD.

This method [63] is applicable to the mixed sulphates as well as to chlorides, the latter being used directly, the former after double decomposition with barium chloride. A small excess of barium is not noxious as barium perchlorate is easily soluble like the other alkaline earth compounds. The possibility of inclusion of potassium in the barium sulphate is detrimental. A primary chloride solution is therefore to be preferred. The liquid is treated in a Pyrex glass dish of suitable size (8—9 cm) with two- or threefold excess of perchloric acid (70 %; sp.gr. 1.12) and is evaporated, until heavy white vapours of perchloric acid are evolved. After cooling, the salts are crushed and intimately mixed with ethyl alcohol, containing 1 % of perchloric acid and saturated with $KClO_4$. This is repeated a few times according to the relative amounts of Na and K, followed by filtration in a sintered glass filter crucible. The potassium perchlorate is washed once with alcohol containing only a trace of perchloric acid. After drying at 120—130°, the perchlorate is weighed.

Factor for KCl : 0.538 ; (0.53801).

K_2O : 0.340 ; (0.33990).

The procedure is to a high degree a compromise method. The filtrate should be preserved for some time, since a correction will have to be applied if further precipitate separates. Pyrex glass should be used in the evaporation as it will not be attacked seriously and contains only 0.20 % K_2O. [64]

CAUTION: It should be borne in mind, that serious explosions are likely to occur when hot perchloric acid comes in contact with organic matter, even in rather dilute solution, or when only the vapours mix. Therefore, procedures giving rise to these conditions should not be employed. The same holds for re-distil-

ling either alcohol or perchloric acid from saved washings; the latter had better be rejected.

Indirect methods for the determination of sodium and potassium (e.g. weighing as chlorides and as sulphates; calculation of the amount of Na and K) are generally worthless as large errors are easily made.

DETERMINATION OF FERROUS IRON. GENERAL CONSIDERATIONS.

There are many pitfalls in the determination of the amount of iron present in the bivalent state. The determination cannot be omitted, however, this value being of great importance petrologically, for the appreciation of the state of weathering of the sample and for the effect on the sum. In the preparation of the sample, the decomposition and the determination, many — grave — errors are possible. In general it may be said, that the simplest and quickest procedure will likewise yield the most nearly correct results.

Errors in the preparation of the sample are mainly due to oxidation, to a lesser degree also to adsorption of moisture. The former defect as well as the latter is overcome largely by crushing — not grinding — the powder to the necessary degree of fineness under alcohol. The portion can be weighed previous to the adsorption of water and oxidation is more or less prevented as, according to HILLEBRAND, it is mainly caused by heat due to friction. The alcohol should be completely expelled before the powder is used in the decomposition. An extremely fine powder is usually required only for the methods of attack with sulphuric acid alone.

In the MITSCHERLICH method, the sample is treated with a mixture of water and sulphuric acid in a sealed tube and an oxygen-free atmosphere at temperatures up to 200°. Errors may be caused by incomplete attack, presence of sulphides, e.g. pyrites and pyrrhotite, and also by too high a concentration of the sulphuric acid. HILLEBRAND has pointed out that 0.01 % of sulphur present as sulphide may cause a plus error in the ferrous iron determination of 0.135—0.18%. This discredits the method for ferrous iron determinations in rocks. [65])

Experiments have shown that the same errors are inherent to a much smaller degree in the hydrofluoric acid method,

mainly as the time, necessary to carry out the decomposition can be made very short and hydrogen sulphide, if produced at all, largely escapes before it reduces ferric-iron. The use of complicated apparatus in the decomposition is generally inconsistent with the requirement of quickness and should be avoided. The sample is decomposed in an ordinary platinum or palau crucible by a mixture of boiling sulphuric and hydrofluoric acids in 5—15'; the escaping vapours prevent the access of the oxygen from the air. Immediately after the decomposition, the liquid is titrated with potassium permanganate solution, if necessary, after having prevented harmful action of the hydrofluoric acid. In the presence of hydrofluoric acid, ferrous iron is easily oxidised by oxygen, especially when the water used for the dilution is not air-free, whilst a definite and constant end-point of the reaction will not be reached as manganous fluoride is gradually oxidized by permanganate. Following a suggestion of Barnebey an addition of boric acid serves as a trap for free hydrofluoric acid, the latter being bound as harmless complex fluorboric acid. [66])

Nevertheless the fact must be emphasised, that the determination of ferrous iron — especially for high percentages and in the presence of large amounts of sulphides — necessarily cannot be as correct, as that of other components. Ordinarily the effect of the errors may be negligible.

DETERMINATION OF FERROUS IRON. PROCEDURE.

To about 300 ml water in a 600 ml beaker of resistance glass, 5 ml of concentrated sulphuric acid are added and the liquid is heated and boiled for a few minutes to expel the air. In the same manner the water in a washbottle is freed from dissolved oxygen. Both vessels are placed in cool water; when cold 10 ml of a saturated boric acid solution are added to the beaker and the liquid is just coloured with a few drops of permanganate solution. In the meantime by a preliminary experiment with the rather coarse rock powder, it is determined whether the ordinary sample is attacked completely within 10—15'. If not, a weighed portion should be crushed under alcohol until the matter is considered to be fine enough. The amount to be taken is decided by the same arguments as in the case of the main portion. 1 g will serve for "acid" or weathered rocks and only

0.5 g for fresh "basic" rocks. Approximately the required amount is weighed in a capacious platinum crucible. (The operation may be carried out in a crucible of 40 ml volume; a palau or other gold alloy crucible will serve admirably). The fine powder is moistened with a few drops of water from the already filled tip of the wash bottle. Then, 10 ml of dilute (1 : 1) sulphuric acid, freshly prepared and consequently still hot, are added to the contents. This is at the same time a qualitative test for carbon dioxide. If much of this constituent is present, the addition of acid should be very gradual and careful to prevent spluttering. The crucible is placed on a triangle at an appropriate height over a very low flame (1.5—2 cm), the latter being protected against draughts by a flame-screen. The height should be so adjusted, that the liquid will not boil violently but enough vapours are liberated to keep away the air. Directly after the crucible is placed on the triangle, about 6 ml of 40 % hydrofluoric acid are added from a platinum crucible, the lid being immediately replaced. Too long an interval after putting the crucible in place on the triangle should be avoided as the reaction with the hot liquid is likely to be very violent then; therefore the hydrofluoric acid should be prepared in time and kept at hand. The flame is temporarily waved at a short distance under the crucible so that the temperature may rise quickly and is lowered again when the liquid is gently simmering. This state should be maintained during the whole attack, the right conditions being easily found after some practice. To prevent the liquid from "bumping" a small piece of platinum foil may be introduced with the powder, but I never have found this to be indispensable. The attack is to be prolonged for the time, shown by the preliminary treatment to be necessary and when the decomposition is considered to be complete — for basic rocks this will require slightly more time, 10—12', whereas for acid or weathered rocks, 5—7' are generally ample — the crucible is taken, preferably with a special platinum tipped instrument, known as BLAIR's tongs and transported as fast as possible to the prepared beaker. The whole crucible is submerged, the tongs withdrawn and immediately washed with water, and the liquid is stirred by means of a solid glass rod, bent at 4 cm from the end at a right angle so as to be able to displace the crucible easily through the liquid.

The liquid is titrated directly with potassium permanganate

solution from a prepared burette. During this titration, the liquid should be thoroughly but gently stirred and the contents of the crucible allowed to mix as completely as possible with the rest of the solution. The titration is finished when the original colour of the liquid has first been perceived for a few seconds — but after thorough stirring. The addition of boric acid, though making the end-point definite and sharp, cannot altogether prevent the colour being bleached subsequently. After the titration, the absence of mineral particles — especially of dark minerals — should be ascertained. If this does not hold, the operation should be repeated, best with a new portion of the sample, but in case of paucity of the latter, with the residue of the first determination. Pyrites, however, should be neglected here. The following errors may be considered: incomplete decomposition is easily avoidable, a correction for sulphides ordinarily cannot be applied accurately, but it may be stated that pyrite is not likely to influence the results as it remains unchanged and can be seen on the bottom of the vessel after titration. If other, soluble, sulphides are present, the hydrogen sulphide generally escapes before exerting a reducing action on ferric-iron; dissolved sulphide-iron, however, will be titrated and erroneously reported as ferrous iron. A correction can be made on the basis of measuring the quantities of soluble sulphides (mostly pyrrhotite) under the ore-microscope with an integration-stage, or by subtracting the "pyrite"-sulphur (determinable in the solids, present in the residual liquid from the titration) from total sulphur and combining the result with the quantity of iron, required to form pyrrhotite: $Fe_{11}S_{12}$. Usually the matter is not of great importance. Trivalent vanadium is likewise oxidised by potassium permanganate; fortunately the amount of vanadium is uniformly very low in rocks, seldom over a few hundredths of a percent. Carbonaceous and other organic matter in large amounts will make the whole determination of ferrous iron of illusory value.

For rocks with ordinary percentages of TiO_2 the titration of ferrous iron with potassium dichromate solution in the presence of phosphoric acid has the advantage of the stability of the standard solution. [67]) As internal indicator diphenylamine can be used, or the titration carried out electrometrically. Addition of three drops of a 0.2 %-solution in sulphuric acid is very suitable also in the titration with permanganate, provided the

trivalent iron is made harmless by addition of enough phosphoric acid. It is unfortunate however, that the same addition is useless in the standardization of permanganate with oxalic acid, the indicator being destroyed during the titration.

The amount of FeO present in the sample is calculated from the required volume of permanganate solution and expressed as percentage of FeO. This, multiplied by 1.111 (1.11133), indicates the value, to be subtracted from the total iron as Fe_2O_3, to obtain the percentage of Fe_2O_3 present in the sample.

DETERMINATION OF WATER. GENERAL CONSIDERATIONS.

The percentage of water is generally reported as divided between H_2O- and H_2O+, respectively indicating the water escaping at temperatures up to 105—110° and water escaping at higher temperatures; the former being largely hygroscopic water, the latter mainly constitutional. It should be remarked, however, that part of the constitutional water in certain minerals, e.g. in zeolites, will be found as H_2O-. If these minerals are absent, a high percentage of H_2O- is often characteristic of weathering; the determination of carbon dioxide and the results of petrographical investigation will yield further evidence on this point.

The different physical states of water in rocks is a matter under discussion by WHERRY, MERWIN and ADAMS in HILLEBRAND'S work [68]) besides being dealt with in a more or less extensive way in treatises on soil science, etc. This need not be repeated here, as chemical methods are not capable of giving further details concerning the state of the water in the sample.

DETERMINATION OF WATER. PROCEDURE.

The total amount of water present in the sample includes: cavity water, hygroscopic water, water in liquid solutions (e.g. in undercooled solutions, glasses), water of crystallization and water, chemically bound in the crystal lattices. Water in all these states is completely expelled when the sample is heated thoroughly with suitable fluxes and usually most will escape

also when the sample is heated alone at high temperatures with a blast, though, in many cases much lower grades of heat will be sufficient. The loss on ignition, however, will not represent the total water, unless no other volatile substances are present (carbon dioxide, sulphur, halides, organic matter) and the sample does not undergo other changes affecting its weight (e.g. oxidation of bivalent iron). Therefore this formerly very frequently used method should be applied only in a very restricted number of cases, where it is certain that other volatilizable matter is absent and the percentage of ferrous iron zero or low (not more than 0,5, at most 1.0 %) A correction for the partial oxidation of this constituent can only be safely made after an exact determination of bivalent iron in the sample after ignition.

Direct methods with absorption tubes are generally not as suitable here, as they are in the determination of hydrogen in organic compounds; the amounts of water present are generally extremely low as compared with the total weight of the tubes and the errors arising through other causes, while the advantageous factor 0.111 in the hydrogen-determination is absent here.

The most suitable method for the determination of water in rocks, many minerals and indeed also for a large number of other substances is the method known as PENFIELD'S, originally described by BRUSH.[69])

A tube of hard glass of 5—7 mm internal diameter and preferably not longer than 15, at most 20 cm (otherwise difficulties will arise in the weighing) is closed at one end, a small bulb being blown there. In the case of the sample containing much water, it will be safe to have another bulb blown in the middle of the length of the tube, where the water is to be condensed. The tube is dried thoroughly by heating it, while a stream of dry air is sucked through by means of a thin glass tube. After cooling, the tube is weighed — 0.1 g of perfectly dry potassium dichromate may be added before weighing; see further — and an appropriate amount of powder is introduced direct in the bulb by means of a filling tube, also dry and clean; the tube is now weighed again. For fresh, crystalline rocks, about 1.0 g of powder will be a suitable amount, for weathered rocks, volcanic glasses and tuffs 0.5 g will serve better. If potassium dichromate has been added, the powders are mixed thoroughly. In the whole operation care should be taken that the powder does not leave the bulb. The open end of the tube is fitted with a small

stopper with a capillary tube to prevent any water vapour being carried away by drafts in the interior of the tube. A moist piece of wadding, filter paper, or cloth is wrapped around the tube at the enlargened part or elsewhere in the middle. The end near the cork is loosely clamped in a stand or may be given a slow rotary motion with the fingers of one hand; the bulb may be slightly higher than the outlet of the capillary tube, to promote the escape of carbon dioxide. The powder is heated, very gently at first especially when much hygroscopic water is present, otherwise it is likely to be blown into the wet part of the tube and the whole operation will have to be repeated. The temperature is raised very gradually to prevent the powder from caking or even melting together with the glass at an early stage, as this will probably yield low values for water. Finally the full heat of a blast may be applied for some time to expel all the water as thoroughly as possible; during the whole time of heating the tube is slowly turned axially, thus preventing the sinking of the softened end and securing uniform heating of the sample. The "condenser" should be moistened repeatedly with cold water.

Next a small but powerful blast flame is directed on the tube, a few mm beyond the bulb. The tube is narrowed and finally drawn off with the aid of a piece of tubing of the same glass, preferably a tube previously used for the same determination. The tube is then cooled while held in a horizontal position and weighed without capillary after it has been cleaned and dried outside. After expulsion of the water by gently heating the tube and at the same time drawing a stream of air through it with the previously mentioned thin tube the apparatus is weighed again. The loss in weight after drying represents total water. Subtraction of H_2O^- yields the percentage of H_2O^+.

The errors are generally negligible indeed the inspection of a test tube for droplets of water after ignition is one of the most sensitive tests for this constituent. The plus effect of carbon dioxide may be avoided by leaving the tube in the balance a few minutes inclined to the open end, the loss in weight by evaporation of the water is a minimum in this short time. The errors introduced by other volatile substances are of remarkably less influence here than with the other methods. If ferrous iron is present in unusually large amounts it may possibly exert a reducing action on the water vapour.[69a] Therefore and to

secure a better decomposition a tenth of a gram of potassium dichromate (dried for some time at 200° and pulverized) may be introduced into the bulb before weighing the tube. Only a relatively small portion should be taken, otherwise it will strongly attack the thin glass walls. The peculiar odour which is often perceived when removing the capillary from the tube, will then be completely absent. For convenience in weighing the tube, a small stand should be available, or a loop of aluminium wire attached to the hook of the balance arm. To retain halides in the bulb and equally to secure a better decomposition, the addition of lead oxide and lead peroxide in the Penfield method has been advocated by DITTLER and HUEBER. [70]) It is doubtful whether these substances will yield entirely satisfactory results; they are now obtainable very pure but the absence of water in them should be ascertained. For small amounts of water a titrimetric procedure — based upon the evolution of HCl by oxychlorophosphines e.g. the naphthyl-compound $C_{10}H_7POCl_2$ — has been proposed by the same authors, following a suggestion of LINDNER, who introduced them into organic analysis. Personally I have always obtained — for high as well as for low percentages — entirely satisfactory results with the PENFIELD method as described above and then the simplicity of the latter will be a distict advantage.

DETERMINATION OF HYGROSCOPIC WATER. PROCEDURE.

For the same reasons as have been given in the former paragraph, the usual methods with absorption tubes will be unsuitable for this determination. Perhaps the titrimetric method [70]) will yield valuable service in this case, but I have no experience with it. As the procedure for the determination of the total amount of water is very accurate and H_2O^- is not of great importance — the order of magnitude being mainly of interest here — the following conventional procedures will be entirely satisfactory.

A somewhat larger portion of the sample is weighed out in a small platinum basin (1—2 g being taken). This portion may be dried, generally at temperatures of 105—110° in an oven, or in a vacuum dessicator over phosphorus pentoxide, or by combining these methods, e.g. at 70—80° over P_2O_5. The former method is

almost universally in use; sometimes a toluene bath is taken for this operation (105°). The loss in weight after cooling of the covered basin in a dessicator is determined and the percentage reported as H_2O^-. The weight will be constant after 30—60' in the oven at 105—110°; when drying over phosphorus pentoxide is preferred in not exceptional cases some weeks may even be required.

The sample is reserved for the determination of manganese (and of phosphorus if desired).

COLORIMETRIC ESTIMATION OF MANGANESE. GENERAL CONSIDERATINS.

For various reasons, the gravimetric methods for the determination of manganese are likely to yield inaccurate, ordinarily high, values when small amounts of this constituent have to be determined in silicates, as will be the case with most rocks. The colorimetric method may be used with advantage for amounts, smaller than 0.5—1. %. Titrimetric methods [72]) are very reliable for percentages of 0.5—5. % and gravimetric methods are entirely satisfactory for amounts larger than 2—3 %. The gravimetric method has been given in detail on p. 61.

In the colorimetric estimation, the sample is decomposed with sulphuric and hydrofluoric acids, the latter is expelled, the filtered solution is treated with some oxidising agent and the permanganate colour is compared with that of a standard solution which has been treated in the same way. If a large number of determinations can be made subsequently, it is of advantage to prepare a colour scale.

COLORIMETRIC ESTIMATION OF MANGANESE. PROCEDURE.

The sample resulting from the determination of H_2O^- is treated in the small platinum basin with 5 ml of 40 % hydrofluoric acid and 5 ml of sulphuric acid, 1 : 1, over a very low flame (to avoid spluttering) protected by a screen. The powder should be stirred with a bent platinum wire to prevent caking. When all the mineral fragments are disintegrated, the hydrofluoric acid is expelled by repeated evaporations with sulphuric

acid, the last time until nearly dry and the residue is dissolved in sulphuric acid, 1 : 1, as completely as possible. (only a small amount of calcium sulphate need remain undissolved — If the determination of phosphorus is intended in an aliquot portion, chlorine-free nitric acid should be used here). The solution is filtered into a small beaker or Erlemeyer through a small filter, or if a portion of the liquid is to be reserved for the phosphorus-determination a measuring flask of 100 ml may be used to catch the filtrate. In the latter case, 50 ml are taken with a pipette, the rest is quantitatively transferred to a 200 ml beaker and the pipette is also rinsed with a few ml of water, the washings being caught in the beaker and reserved for the phosphorus-determination.

The oxidation of the manganous salt is carried out in strongly acid solution by the addition of 0.3—0.4 g solid potassium periodate, or — as this salt is difficult to obtain, at least in Europe — by solid potassium persulphate with silver nitrate as catalyst. The colour is compared with that of a standard solution, treated in the same way. Direct comparison with standard permanganate solution will be suitable for small amounts (a few 0.01 %) but not for larger as the colour-tone of the two solutions is decidedly different. A solution of $MnSO_4$ is prepared by reducing an acid solution of potasium permanganate with sulphurous acid or sodium sulphite and diluting to a concentration of 1 mg MnO/10 ml. The solution of silver nitrate should have a strength of 0.5 % and 10 ml are required for every 2 mg MnO in the sample.

To the liquid in the beaker or in the flask is added the required amount of silver nitrate solution and enough sulphuric or nitric acid to obtain a solution with 10 % by volume of sulphuric or 30—30 % by volume of concentrated nitric acid. Then, 1—2 g of potassium persulphate are added in the form of a freshly prepared 10 % solution and the flask is heated gently. The pink colour will soon appear and increase gradually. The excess of persulphate may be destroyed by boiling for a few minutes and then the flask is placed in cold water or cooled under the tap. From the standard solution enough is taken — in multiples of 10 ml — to get a somewhat darker colour and both solutions are compared. This may be carried out in a colorimeter, in Nessler glasses or when a scale is used, in a number of test-tubes of about the same diameter.

A brown colour, or even precipitate is frequently observed under wrong conditions, e.g. lack of sufficient silver nitrate or, more likely, insufficient acidity of the liquid and can usually be overcome by the addition of more of one of these if necessary after reduction with sulphurous acid or sulphite. Should perchance, on the addition of silver nitrate a precipitate be formed, which is not likely to occur as chlorine will be expelled when the decomposition has been carried out properly, the turbid solution should be filtered into a clean vessel and more silver nitrate added.

The same procedure will be followed with the magnesium pyrophosphate and perhaps with the ignited oxalate precipitate to apply a correction for co-precipitated manganese. In the latter case this correction may be done on the basis of Mn_3O_4 in the precipitate. In the magnesium-determination, manganese is weighed as pyrophosphate, so the amount of MnO is multiplied by 2, (2.001) to obtain the weight as pyrophosphate.

The errors are negligible. The oxidation may also be done with 0.5 g of lead peroxide but this is not advisable as the comparison necessitates a filtration of the suspension through asbestos to remove the undissolved peroxide.

DETERMINATION OF PHOSPHORUS PENTOXIDE. GENERAL CONSIDERATIONS.

Phosphorus can be determined in many stages of the analysis, but preferably in a separate portion. Further, it can be investigated in the joint precipitate with aluminium in the main portion if paucity of material urges the analyst to have recourse to this procedure. Or an aliquot portion may be taken from the solution, obtained in the course of the colorimetric determination of manganese. The determination in the main portion is not to be recommended as part of the phosphorus will be co-precipitated with Ti or Zr in the silica-determination and some loss is to be expected in the treatment of the ignited silica.

DETERMINATION OF PHOSPHORUS PENTOXIDE. PROCEDURE.

Though the minerals containing phosphorus are all soluble in even dilute nitric acid, the decomposition is best carried out

in the following manner, as other minerals may contain *inclusions* of apatite and the like. An amount of "*a*" g of the sample (cf. decomposition of the main portion) is treated in a platinum crucible with a mixture of equal amounts of 40 % hydrofluoric acid and dilute nitric acid, 1 : 1, to decompose the minerals and to eliminate the silica. This operation can be done as has been described for the decomposition under "manganese". The hydrofluoric acid is thoroughly expelled by repeated evaporations with nitric acid on the water-bath [73]; the last time, a ml of ammonium nitrate solution may be added to serve the same purpose. Finally the dry contents of the crucible are mixed thoroughly with (5 a + 2) gram of *potassium* carbonate and the fusion carried out as has been described for the decomposition of the main portion. After cooling, the mass is dissolved in a small volume of water and the solution is filtered off from the solid matter. The liquid is acidified with nitric acid in a tall beaker, covered with a watch glass and evaporated down in a basin to less than 50 ml. To the still hot solution are added 25 ml of ammonium nitrate solution, 1 : 3, and the liquid is brought to the boil. A mixture of 20 ml of ammonium molybdate reagent and 20 ml dilute nitric acid, 1 : 3, is warmed slightly (40—50°) and — while the other solution is thoroughly stirred — is poured into the beaker. The precipitate is allowed to stand for about 6 hours and is then filtered into a porcelain or glass filter crucible. The aid of a rubber-tipped glass rod may be useful or necessary to loosen the precipitate from the walls of the beaker. In the case of rocks it will be hardly necessary to convert the phosphorus in the precipitate into magnesium pyrophosphate. So, the precipitate is washed thoroughly with 1 % nitric acid and dried at 105°. Its composition is approximately : $(NH_4)_3PO_4.12\ MoO_3$.

Factor for P_2O_5 : 0.0375 ;
for P : 0.0164.

After the precipitate has been dissolved in dilute ammonia, 1 : 2, the crucible is dried and weighed and, if desired, the amount of phosphorus can be checked in the liquid — after filtration — by double precipitation of magnesium ammonium phosphate, followed by ignition to pyrophosphate. This operation — the inverse of the determination of magnesium — is described in the section on the analysis of phosphates, p. 169. The solution is acidified with HCl; then, 10 ml of acid magnesia mixture are added and ammonia is added dropwise until the

boiling liquid smells faintly "alkaline". For further treatment see under magnesium p. 69.

DETERMINATION OF CARBON DIOXIDE. GENERAL CONSIDERATIONS.

Carbon dioxide is a constituent which will seldom be found in unaltered igneous rocks. Through weathering, carbonates increase rapidly at first, to be dissolved in the later stages of this process, but this cannot be misunderstood as in these later stages the decomposition of the rock as such is almost complete, laterites, clay-substances or other soil types being formed. It should be borne in mind, that by volcanic actions, occurring in later stages of magmatic cycles — pneumatolytical and especially hydrothermal stage — solutions, rich in carbon dioxide, may bring about the occurrence of carbonates, frequently associated with zeolites (cf. water; general cons.) A simple test for the detection of carbon dioxide in small amounts has been given on p. 39.

DETERMINATION OF CARBON DIOXIDE. PROCEDURES.

Fig. 7.

Approximate method for very small percentages of Carbon dioxide. In case of *very* small amounts being present, the volume of the gas, set free by acids may be estimated, and the amount of CO_2 calculated on this basis. An apparatus which serves quite well for this estimation has been described by STRUYCK for fermentation experiments, (fig. 7) [74]. 1—3 g of the rock powder is weighed out and placed in the lower tube. Freshly boiled water is added until the tube is half full and the powder entirely covered. The liquid is boiled to drive out the air from the surface of the powder and after cooling, the whole apparatus is filled with freshly boiled water. Sulphuric acid, 1 : 1, or concentrated hydrochloric acid is placed in the upper tube, the flask being held in an inclined position. The heavy acid partly displaces the water in the lower tube. The carbon dioxide collects in the upper part of the lower tube. The apparatus may be graduated under the same condition, with known amounts of *granular* calcium carbonate (marble).

For larger percentages, the fragile apparatus designed by

BUNSEN, RUPP and others [75]) — in which the loss in weight of the sample by the expulsion of CO_2 is ascertained, taking care to absorb any water vapour — are not to be preferred as carbon dioxide is easily determined by direct weighing. Other indirect procedures, e.g. loss on ignition, are sometimes suitable for carbonate rocks and minerals; for the general principles which determine in any special case the applicability of these methods, see the general considerations for the determination of water on p. 88 and 89.

Therefore, the well known absorption train should be used when a considerable amount of carbon dioxide is present (more than 0.2—0.5 %). The sample is preferably decomposed in a decantation flask (fig. 10, C) of Jena glass, from 1—5 g being taken, according to the expected percentage of CO_2. The flask is provided with a two-hole stopper, one of these holes bearing an inlet-tube, the other being supplied with a wide vertical tube with water-cooler. The vertical tube is bent at the upper end and is connected with the train of absorption tubes: 1. a tube containing pumice with anhydrous copper sulphate, 2. a calcium chloride tube — the contents of this tube are to be neutralized carefully to prevent retention of the expelled carbon dioxide. — 3 and 4, U-tubes for three fourths filled with soda lime or ascarite and for the remaining fourth part with crude calcium chloride. An aspirator is connected to 5. a safety tube filled with calcium chloride. The aspirator can be replaced by a large flask connected to the water-pump.

The connections are made "glass on glass" with thick-walled rubber tubing to prevent diffusion of carbon dioxide. When the whole apparatus has been assembled, the tightness of the connections is tested by applying suction whilst the inlet-cock remains closed. No flow should be indicated after the equilibrium has been reached.

Enough dilute hydrochloric acid is added, so that the inlet is under the surface of the liquid and the latter is brought to a boil, the aspirator being put into action in the same time. After 10—15' gently boiling, the flame is removed the suction being still applied for another 15'. At the end of this time the connections are loosened, the absorption tubes with soda lime are weighed after temperature equilibrium has been reached in the balance case and the gain in weight is reported as CO_2. The air stream used in this determination should be free from CO_2; a

piece of rubber tubing to the free air will supply this, provided the stream of air is not made too rapid, but this should be avoided for other reasons as well. The anhydrous copper sulphate serves to retain any hydrogen sulphide and hydrochloric acid.

If minerals containing CO_2 and insoluble in dilute hydrochloric acid are present, the powder should be very fine and a few ml of hydrofluoric acid should be added. In the case that manganese dioxide is present, e.g. in soils or in weathered basic rocks, hydrochloric acid should be replaced by dilute sulphuric, phosphoric or acetic acid to prevent evolution of chlorine.

Cf. DIXON's method for the determination of carbon dioxide and carbon or carbonaceous matter in one portion of the sample, p. 131, fig. 10.

DETERMINATION OF CHROMIUM, TOTAL SULPHUR, BARIUM, ZIRCONIUM, RARE EARTHS. GENERAL CONSIDERATIONS.

The determination of these five constituents is most conveniently carried out in one portion of about 2 g, according to the procedure of HILLEBRAND.[76] The sample is fused with carbonate and nitre — the latter to oxidize sulphide-sulphur — and the melt is taken up in water. Of the constituents under consideration, chromium and sulphur go into solution respectively as chromate and as sulphate. Chromium is estimated colorimetrically in this solution after destruction of the manganate by alcohol, followed by precipitation of the sulphate with barium chloride. The residue from the leaching with water is acidified with sulphuric acid to precipitate the barium as sulphate. This is filtered off, purified and weighed. In the acid solution, zirconium is precipitated as phosphate, titanium being kept in solution by oxidizing it with hydrogen peroxide.[77] The rare earths are next precipitated, together with iron and titania, by enough sodium hydroxide solution, to keep aluminium and phosphorus in solution. The precipitate is treated with hydrofluoric acid to obtain the insoluble fluorides of the lanthanides. After purification, the rare earths are weighed as oxides. A separation into the elements, or even the groups, will rarely be succesful.

DETERMINATION OF CHROMIUM, TOTAL SULPHUR, BARIUM, ZIRCONIUM AND RARE EARTHS. PROCEDURES.

About 2 g of the sample are mixed with 8—10 g of potash and not more than 0.5, at most 0.75 g of potassium nitrate, otherwise the platinum crucible may be strongly attacked. Carbonate and nitrate should be entirely free from sulphur compounds. The fusion is carried out very cautiously at first; owing to the reaction between the constituents of the flux, more effervescence will take place here than in the ordinary attack with carbonate only. The flame gases are kept away from the contents of the crucible by inserting the latter in an exactly fitting hole in an asbestos shield to prevent contamination with sulphur. Further, the operation is carried out as has been described for the decomposition of the main portion; an electric furnace will be valuable here too.

CHROMIUM.

The cold cake is dissolved in a minimum of water — so, if sufficient pure potassium carbonate can be procured, this is to be preferred to the sodium salt — a few drops of alcohol are added to destroy the manganate colour. The liquid is filtered by decantation through a small filter (7 cm). The analyst should try to get as little of the precipitate as possible, on the filter. Both, residue and filter, are washed thoroughly with 2 % sodium carbonate solution. The portions of washing liquid should be small, to keep the volume of liquid less than 100 ml. If a yellow colour is visible in the clear liquid, chromium is estimated colorimetrically, using a standard solution of potassium chromate for comparison.

SULPHUR.

After the colorimetric comparison for chromium, the liquid is transferred quantitatively to a 400 ml beaker and is coloured with a few drops of methyl orange solution. The beaker is covered and concentrated hydrochloric acid is added in slight excess, using small amounts at a time. The colour should indi-

cate neutrality, after which 1 ml of 0.5 N hydrochloric acid may be added. The liquid is heated gently at first, to drive out the carbon dioxide and, when the boiling point is reached, 10 % barium chloride solution is added until no more precipitate is formed. Then, 1 ml of the solution is added in excess and the liquid is kept hot for some hours. After cooling, the beaker is allowed to stand overnight and the precipitated barium sulphate is filtered off. If the liquid has been kept hot long enough, an extra fine-grained paper will not be required. A rubber-tipped glass rod will often be necessary to clean the walls of the beaker. The filter should be as small as feasible and care should be taken not to over-wash the precipitate. The filter is charred at a very low temperature and the carbon oxidized also at a moderate heat (dark red), otherwise mechanical losses are unavoidable and reduction of the sulphate may take place. The final heating after the whole mass is white, should be done at a temperature of 900—1000°. For larger amounts, the sulphate may be purified by fusion with carbonate, aqueous extraction of the cake and reprecipitation with barium chloride solution. The amounts of sulphur usually found in rocks do not warrant this refinement.

Factor for SO_3 : 0,34286.
for S : 0,13730.

BARIUM.

The insoluble residue of the fusion cake contains (as far as concerned here) the elements barium (carbonate), zirconium (as alkali zirconate) and rare earths (oxides or carbonates). Zirconium and rare earths are brought into solution by treating the mass with sulphuric acid. The whole residue will dissolve readily, leaving behind only the barium as sulphate.

Therefore, the filter paper which has been used, containing the least possible amount of the residue is rinsed with a fine jet of the wash bottle and the liquid is caught in the vessel containing the main mass. The contents are acidified, 1—2 ml sulphuric acid being added in excess and the beaker is covered to prevent loss by spluttering. The liquid is gently heated, the barium sulphate is filtered off, the filter is carbonized and the mass is fused with rather large excess of sodium carbonate. The cake is dissolved in water, the carbonates are filtered off on a small

filter (5½ cm) and dissolved in dilute hydrochloric acid. The filtrate is caught in a clean beaker, diluted to 100—150 ml — to prevent co-precipitation of strontium — and 1 ml diluted sulphuric acid, 1 : 1, is added. The further treatment has been described for the determination of sulphur. Factor for BaO : 0.66. (0.65705).

The purification is required to separate silica, iron and strontium from the barium sulphate.

ZIRCONIUM. (and TITANIUM if desired).

The sulphuric acid filtrate of the barium sulphate contains a large number of constituents of the original sample. Zirconium is quantitatively separated as phosphate while the titanium is prevented from co-precipitation by the addition of a sufficient quantity of hydrogen peroxide. The solution obtained after oxidation may be colorimetrically compared with a standard solution of titanium, but only previous to the subsequent addition of phosphate as this has a marked bleaching effect on the yellow colour. Therefore the liquid is acidified with 10 % of sulphuric acid by volume, treated with 5 ml of 30 % hydrogen peroxide and after the optional control-estimation of titanium, there is added 10 ml (10—100 fold excess), of a 10 % solution of alkali — or ammonium phosphate and the beaker containing the liquid is allowed to stand overnight. The precipitate is filtered off, at first by decantation, on a small filter; filter and precipitate are well washed with a 5 % ammonium nitrate solution. Cautious ignition, according to the same principles as prescribed for magnesium pyrophosphate or barium sulphate, yields ZrP_2O_7. Factor for ZrO_2 : 0.465. *)

As the zirconium phosphate is generally very pure, a further treatment is not necessary. If, however a contamination is feared,

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*) Treadwell (Lehrbuch II, 11. Aufl. (1935), p. 432) gives the factor 0.518.
Jakob (Anleitung, (1928), p. 63): the same factor. (0.518).
Washington (Manual, 4th. ed. (1930), p. 258, 277) gives the factor 0.432.
Dittler (Praktikum, (1933), p. 63): the same factor, (0.432).
Hillebrand (Bull. 700. U.S.G.S., p. 174) gives the factor as correctly as can be expected with the old atomic weight for zirconium, namely 0.463.

the precipitate is fused with sodium carbonate, the cake leached with water, the insoluble residue filtered off and after ignition of the filter paper, the residue is fused with potassium pyrosulphate. The cake is dissolved in sulphuric acid, 1 : 5, and the precipitation with phosphate is repeated. After this fusion with pyrosulphate, as an alternative, zirconium may be precipitated with cupferron, using THORNTON's method, (as described for titanium, p. 58, seq.) and weighed as ZrO_2.

RARE EARTHS.

The rare earths are determined in the filtrate from the zirconium phosphate. This is neutralized with a 10 % sodium hydroxide solution, more of the precipitant being added in a quantity, just sufficient to re-dissolve the precipitated aluminium phosphate. The rare earths are now in the precipitate, together with iron and titanium. After filtration and repeated washings, at first with sodium carbonate solution and followed by hot water, the precipitate is rinsed into a small platinum basin, a few ml of hydrofluoric acid are added to convert the hydroxides to fluorides and the liquid is evaporated. In another basin or a platinum or palau crucible, a very dilute hydrofluoric acid solution is prepared and the dry salts are dissolved in the least possible quantity of this liquid. The insoluble rare earth fluorides are filtered off on a small filter in a platinum funnel. In place of platinum, bakelite will serve equally well. The filter is thoroughly washed with the hydrofluoric acid solution and is then ignited with its contents. After conversion to sulphates, followed by expulsion of the excess of sulphuric acid, a hydrochloric acid solution of these sulphates is prepared. A slight excess of ammonia precipitates the lanthanides as hydroxides; these are dissolved in hydrochloric acid and in the now pure hydrochloric acid solution of the rare earths, the latter are precipitated in dilute acid solution with an excess of ammonium oxalate. After filtration through a small filter ($5\frac{1}{2}$ cm), the precipitate is ignited and weighed as mixture of the oxides. Though cerium and perhaps other rare earths may be present in the tetravalent state, a reduction is not called for with the generally very small amounts. The oxides are to be reported as „RE_2O_3" or $(Ce,Y)_2O_3$.

A group separation is only possible when larger quantities of

lanthanides are present; this may be the case in several minerals. The oxides are then dissolved in a minute quantity of dilute hydrochloric acid, evaporated down, dissolved in a few drops of water and treated with 2—3 ml of a saturated potassium sulphate solution prepared beforehand and in equilibrium with the solid salt. A difficultly soluble double sulphate of potassium and cerium separates and is filtered off. Reprecipitation with ammonia and ignition of the hydroxide yields CeO_2, Factor for Ce_2O_3 : 0.95.

The yttrium-group is determined by difference or directly after actual precipitation with ammonia.

CORRECTIONS IN PERCENTAGES OF OTHER CONSTITUENTS FOR ELEMENTS OF THESE GROUPS.:

The percentage of *aluminium* is affected by the sum of chromium, zirconium and rare earths. Consequently, a corresponding correction should be applied. Barium should be removed in accurate analyses before the precipitation of magnesium as phosphate, as a correction cannot be safely applied. Sulphur does not interfere with other constituents. *Total sulphur* is to be corrected for sulphate sulphur, to obtain sulphide sulphur. Sulphide sulphur displaces oxygen. An equivalent amount of oxygen is to be subtracted from the sum, for example:

0.20 % S present in $Fe_{11}S_{12}$:	0.81 % S present in FeS_2
(iron counted as FeO)	(iron counted as Fe_2O_3)
O less for S : $11/24 \times 0.20$ %	O less for S : $3/8 \times 0.81$ %
= 0.09 %	= 0.30 %

DETERMINATION OF SULPHUR TRIOXIDE. GENERAL CONSIDERATIONS.

The determination of total sulphur has been described in the foregoing paragraph. This represents SO_3 as well as oxidized sulphide sulphur. When sulphides are absent, the whole is to be reported as SO_3; this will be seldom true and the other case will more frequently be met, namely that sulphides alone are present. Microscopical examination of a slide and of a polished surface will reveal the particular sulphur-minerals which are present in the sample. When sulphides and sulphates occur

together, soluble sulphates can ordinarily be extracted by boiling with water, while boiling dilute hydrochloric acid — preferably in a carbon dioxide atmosphere — dissolves more difficultly soluble sulphates as well as complex silicates containing sulphur trioxide (some feldspathoids). The sulphur of acid soluble sulphides is liberated as hydrogen sulphide and may be determined by precipitation as some insoluble sulphide. Difficultly soluble sulphides are oxidized to sulphate with suitable reagents e.g. aqua regia and bromine; insoluble sulphates are decomposed by fusion of the residue obtained from these extractions with sodium carbonate.

The procedure for the separation and exact determination of *larger* amounts of sulphates will be given in a further chapter (p. 162); the procedure for the determination of the sulphur trioxide is described on p. 99 and 162.

Factors for conversion: $S : SO_3 = 0.40046.$

$SO_3 : S = 2.4975.$

Further Constituents of Igneous Rocks.

Other constituents have also been determined or detected in igneous rocks. e.g.: Li, Be, B, NH_4, F, SO_3, Cl, V, Co, Ni, Cu, Zn, As, Ag, W, Au, Pb, Ra, U, platinum metals, etc. Ordinarily the methods of concentration and determination — if only traces are present — are so complex, that it is far beyond the scope of this book to deal with them and furthermore, spectrographic methods are more appropriate here. Exceptions may be made in the case of lithium, beryllium, boron, fluorine, chlorine and sulphur trioxide. The determination of these constituents will be dealt with in the section devoted to the analysis of silicate minerals; methods for the determination of other elements in large percentages see chapters on the analysis of salt deposits and ore minerals, (cf. index).

Mineral Analysis. General Considerations.

The analysis of minerals is a task often facilitated by the relatively simple composition of many minerals, but sometimes complicated by the elaborate procedures involved in the prepa-

ration of a sufficiently pure sample and the separation of some less common elements in larger quantities.

First of all the name of the mineral or at least the group to which it belongs should be determined by a mineralogical investigation. Optical methods are most suitable here. There are especially two tables [78]) for the determination of non-opaque minerals which will be useful to the analyst or rather to the mineralogist with whom the analyst should collaborate in this matter, if both qualifications are not united in one person. This ordinarily will give sufficient indications as to the group, or species of the mineral under investigation and then the chemist should have recourse to former analyses or geochemical considerations or better spectrographic analysis, to ascertain the necessity or desirability of quantitative search for still other constituents. This preliminary work being done, the next task of the analyst will be to procure an amount of the pure mineral, enough to be able to perform all the necessary separations. If but a given amount is available, the chemist should make use of it in the most efficient way and try to determine as many constituents in every portion of the sample, as possible. This will often take much more time than the routine procedures and give a chance of confusion, but the analysis of a mineral is a task, upon which more labour should be spent than on the analysis of rocks which often vary considerably within narrow areas, so that their general chemical character is of much more importance, than minor differences. This, however, is by no means the case with minerals, where the calculation of a formula requires a very accurate analysis.

As an example of a combination of determinations in one portion that will ordinarily not be preferred by most analysts for adequate reasons, the determinations of the elements of the main portion together with the alkalies after the decomposition by fusion with boric acid according to JANNASCH may be mentioned. [79])

It will often be much better, either to try to obtain more of the sample, or to work with smaller portions. Semi micro-analyses can be carried out in almost every laboratory with saving of time and material and without very drastic precautions, provided, a micro-balance or semi micro-balance is available. Concordant results have been obtained by the author even with an ordinary analytical balance, attempting to guess the .01 mg by

noting the turning points of the pointer, in analyses of albite and even silicate rocks with portions of 0.1 g for the main fusion and the alkali determination. It should be pointed out, that for other portions these small amounts are far less satisfactory and that consequently, the total gain or better "loss" is but small.

Thus it will be advisable to purify as much of the mineral as possible and as will be necessary for the determinations intended. One is likely to meet grave difficulties, due to the inclusions of and intergrowth with other minerals, glassy particles of liquid inclusions. As a rule, the safest way is to diminish the grain-size to less than that of the contaminating constituents and separate the latter from the mineral under investigation by chemical or physical methods.

It would go beyond the scope of this book to give complete details of the procedures in question [80]) As most of these methods are essentially simple to carry out, a brief description will suffice.

MINERAL SEPARATIONS. TREATMENT BY CHEMICAL AGENTS.

After thorough pulverization, either the mineral to be removed, or the mineral to be analysed may be easily soluble in some reagent, whereas the other group will resist the same treatment. E.g. carbonate minerals are generally separated most conveniently from others — both of magmatic or sedimentary origin — by a treatment with dilute acid, this being at the same time the method of decomposition for the sample. The insoluble residue is to be investigated separately or discarded after its weight has been determined and if necessary also the loss on ignition. In other cases, the undesired component, may be dissolved in appropriate reagents, e.g. chalcedony in dilute caustic alkali or carbonate solution, carbonates in acids, salt incrustrations in water, etc. etc.

MINERAL SEPARATIONS. PHYSICAL METHODS.

As a rule, these methods are less satisfactory than chemical, not in themselves, but owing to the difficulties of avoiding fine dusts sticking tenaciously together, or the particles may be composed of more than one mineral-species. They can be divided as follows:

1 Hydraulic methods: panning and flotation methods and those used in the so-called mechanical analysis of soils, etc.
2 Static heavy liquid separation.
3 Magnetic methods.
4 Electrostatic methods.

1. The hydraulic methods afford a separation through the agency of two properties of the material: shape and specific gravity. They therefore serve best the separation of compact dense matter from light substances with large surfaces as compared with their mass. If, however, the specific gravities of the substances to be separated differ considerably, a fairly accurate separation by this property can be secured: e.g. gold- or diamond-washing, secondary cassiterite deposits and other natural heavy mineral concentrates.

2. A theoretically more exact separation is afforded by the methods making use of heavy liquids. [81]) Of late, the application of the centrifuge has appeared to be a valuable improvement, as quick and accurate separations have been made of substances differing only .01 in spec. gr. Centrifuges have even been constructed with electrical heaters for heavy "liquids" which are solid at ordinary temperatures. In this, as well as in the other physical methods an excessive quantity of dust should be avoided, so the sample should be sieved frequently during the pulverization and a panning procedure can be applied in this case — not when the whole sample is to be analysed — to remove the dust-portion. A number of heavy liquids are available and may serve for several separations. Ordinarily, they are diluted with water or — those of organic nature — with organic liquids such as benzene or xylene or chloroform, to yield the specific gravity, required for the special purpose. The liquids most employed are enumerated below:

Ethyl iodide	1.93
Bromoform	2.90
Acetylene tetrabromide, Muthmann's liquid	2.97—3.00
Potassium mercury iodide solution, Thoulet or Sonstadt's solution	3.19
Cadmium boro-tungstate solution, Klein's liquid	3.33
Methylene iodide	3.33
Methylene iodide, saturated with iodoform	3.45

Barium mercury iodide solution	
Rohrbach's solution	3.5
Thallium formiate and malonate,	
Clerici's solution	4.06
Mercury nitrate-hydrate, Retgers' solution	4.3
Thallium nitrate — silver nitrate (Retgers)	4.5 at 75°
Thallium nitrate — mercury nitrate	5.3 at 76°

It is to be remembered that generally, the organic liquids are most suitable owing to their low viscosity and because the sample is easily cleaned by washing with benzene or xylene. In addition, these liquids are noncorrosive and only slightly poisonous. The same cannot be said of the inorganic solutions. THOULET'S liquid severely attacks the skin and other organic substances such as rubber. Consequently apparatus entirely in glass should be used throughout in operations with this solution. There are numerous observations regarding the attack of the minerals to be separated by the heavy solutions. Replacements of metallic constituents of minerals, especially by thallium, have been observed. In general, the separation of substances yielding an alkaline reaction is impossible owing to the acid reaction of many of these solutions. Carbonates are likewise apt to cause errors but these are easily overcome by first treating the sample with dilute acids. The solid salts should not be exposed to prolonged heatings, nor should the temperature rise too high, as they are slowly decomposed at their melting points and quickly at 100°. Finally the thallium silver nitrate attacks sulphides, consequently samples containing these minerals should be separated either with mercuric nitrate-hydrate or with the mercuric thallium double salt. The inorganic liquids or melts are easily regenerated by evaporating them to their original or maximum density. The organic liquids require fractional distillation to be purified.

3. Magnetic methods are especially suitable for separating magnetite, titano-magnetite and pyrrhotite from slightly magnetic or dia-magnetic minerals. With an electromagnet, weakly magnetic substances can also be separated, but the operation can hardly be considered to be quantitative. The magnetic method can be applied with much advantage to separate small splinters of iron derived from the steel mortar from otherwise non-magnetic samples.

4. Electrostatic methods have not yet found considerable application in the laboratory practice of mineral separations.

It is obvious, that often a better separation and a purer portion for the analysis may be obtained after more than one operation with *different* methods.

The pure sample is stored in a clean, dry bottle after equilibrium has been reached with the water-vapour pressure of the air. It is preferable to determine the specific gravity previously. The correct estimation of this value requires painstaking care. In exact determinations, a correction for buoyancy should be applied. In mineral analysis the determination of the density should never be omitted.

Determinations of optical, crystallographical and other physical constants should be made on appropriate parts of the sample.

SILICATE MINERALS. GENERAL CONSIDERATIONS.

Many silicate minerals are soluble in acids (without preceding decomposition with carbonate melts) either after, or without fusion or sintering of the sample. This behaviour should always be borne in mind, as considerable saving of time can be made by decomposing with acids instead of fluxes and less contamination by alkali salts need be feared in this case. Cf. p. 40 and the sections on analysis of coal and plant ash.

There are a large number of minerals, which, though the general course of analysis need not be very different from that for silicate rocks, require special provisions for the determination of elements which have not been mentioned hitherto because of their rareness in most rocks. These elements are: lithium, beryllium (= glucinum), boron, fluorine, chlorine, vanadium, nickel, thorium and uranium. This series does not cover the whole range of possible silicates, but the elements which have been omitted either yield quantitatively quite unimportant silicates, or compounds which can easily be analysed when the chemist is acquainted with the methods of silicate analysis and with the determination of the metals in question e.g. in the case of Willemite (Zn-silicate).

The above elements generally need not be determined in the analysis of minerals derived from ordinary igneous rocks. In the so-called *alkali-rocks,* however, especially when rich in sodium, the elements lithium, beryllium, fluorine, chlorine, zirconium, rare earths and hafnium are not rare and may be locally

concentrated. Associated with granitic rocks occur pegmatites, sometimes rich in boron, fluorine, niobium, molybdenum, tin, tantalum, tungsten, thorium and uranium. Finally, in highly ferro-magnesian rocks there are often found local concentrations of minerals with higher percentages of the elements: phosphorus, titanum, vanadium, chromium, manganese, nickel and copper, or these elements may be found in smaller percentages spread throughout the whole body of the rock.

In *metamorphic rocks* of sedimentary origin, it is often worth while to make a determination of boron and the same holds *a fortiori* for minerals separated from these rocks. Boron is taken up during the formation of sediments on the bottom of the sea and nearly the whole amount enters into the composition of definite minerals.

In cavities in igneous rocks and on the walls of clefts in the surroundings of magmatic bodies, minerals are often found which do not belong directly to the rocks of the magma of these igneous bodies, but are nevertheless related with them in the same magmatic cycle. These minerals represent a much larger variability in composition than true igneous minerals, but within the limits, drawn by the possibilities of the elements present in the magma.

DETERMINATION OF LITHIUM. GENERAL CONSIDERATIONS.

Lithium, if present in amounts, warranting its quantitative determination can always be detected with a simple hand-spectroscope.

Its presence does not merely affect the determination of the alkalies, but also that of the elements in the ammonia precipitate, as lithium salts, when present in more than traces, are tenaciously adsorbed in this precipitate and ordinarily three precipitations are required to free it from lithium. [82]) The traces that still persist are removed during the ignition of the precipitate.

As pure lithium compounds attack platinum considerably if they are fused in vessels of this metal, (due to formation of LiOH) fusions with high concentrations of lithia are to be avoided. Ordinarily one need not fear attack of the crucible in the main fusion, but in the decomposition for the alkali determination it

will perhaps be safe to make use of an iron or porcelain finger crucible although I have not found any damage after three succesive fusions in platinum.

Lithium has a slight tendency to form basic salts; therefore, sufficient quantities of chlorine ion should be present throughout the whole process. For the same reason, JAKOB [83]) recommends that the decomposition according to L. SMITH be repeated with the dried residue from the extraction, when larger quantities than a few mg of lithium are present. This, however, seems superfluous, as LiOH is not very insoluble, so that the small quantities present, generally are easily dissolved during the repeated extractions with water.

Lithium accompanies sodium in the analysis, so, after a preliminary attack, followed by separation of potassium, lithium is found together with the sodium of the rock and perhaps some magnesium in the filtrate. Both metals are separated by making use of the different solubilities of their chlorides in organic solvents, e.g. pyridine, ether-alcohol, and amyl alcohol.

Lithium minerals are: lepidolite (silicate; mica), spodumene (silicate), amblygonite (phosphate), petalite, and triphylite. It is found in smaller percentages in lithiophyllite, felspars, muscovite, beryll and other minerals in isomorphous replacement, often for magnesium.

DETERMINATION OF LITHIUM. PROCEDURE OF AMYL ALCOHOL METHOD. [84])

The determination of lithium is preferably done after the separation of potassium as chloroplatinate in the filtrate. Therefore the platinum in this solution is removed as has been described on p. 82 by introducing hydrogen into the boiling solution. As an alternative, the separation by hydrogen sulphide may be mentioned. The final solution should be colourless and is evaporated down to a small volume. Purified amyl alcohol is added (about 20 ml for 0.2 g of mixed chlorides in a small beaker or flask, from 100 ml) and a small piece of platinum foil is put in the liquid to prevent bumping. The heating is now continued, the water is removed and the temperature will gradually rise until the boiling point of amyl alcohol is reached (130—132°). By this operation NaCl (if the operation has been done on a

mixture of LiCl + NaCl + KCL, also the latter) and some LiOH are thrown out and to reconvert the lithium hydroxide to chloride, add two or three drops of concentrated hydrochloric acid after cooling the solution. By again heating the liquid, the last traces of water are removed. Cool the flask until it can be conveniently handled and filter the hot alcohol into a graduated cylinder through a filter crucible. If large amounts of lithium chloride are present (more than 20 mg), it may be included in the separated chlorides. In this case, the salts are dissolved in a few drops of water and a second treatment according to the described procedure will dissolve the last traces of the salt. The chlorides in the crucible are washed with small portions of amyl alcohol at a time after every separation. These washings are not caught in the measuring cylinder. The crucible and contents are dried directly over a low flame and weighed after cooling in a dessicator.

The filtrates and washings are evaporated to dryness in a small platinum or porcelain dish at a temperature of not over 125° to prevent bumping. The residue is washed with as small portions of dilute sulphuric acid as possible into a platinum crucible and the liquid is evaporated until it fumes. When not entirely free from organic matter, the evaporation with small portions of dilute sulphuric acid is repeated. Finally the solid salt is fused for a short time and the covered crucible is cooled in a dessicator and weighed as quickly as possible. Lithium salts are very hygroscopic.

Corrections have still to be applied for the solubility of NaCl (possibly also KCl) in the hot amyl alcohol. For every 10 ml of filtrate (washings not included)add 0.41 mg of NaCl or 0.51 mg of KCl if but one of the chlorides is present and 0.92 mg if *sufficient* quantities of *both* were in the mixture. The correction for the weighed lithium sulphate is made in the same way: subtract 0.50 mg for sodium sulphate, 0.59 g for potassium sulphate if these salts are present alone, or 0.09 mg for every 10 ml of filtrate when both salts are present. Factor for Li_2O : 0,27186.
for LiCl : 0.77125.

In working up large quantities of mixed chlorides to determine traces of lithium in them, as will for example be the case in the analysis of mineral waters, it will be convenient, to separate potassium and sodium chloride now and then during the process by precipitating them with a current of gaseous hydro-

chloric acid, generated in a suitable apparatus and purified by washing with a small quantity of concentrated hydrochloric acid, followed by sulphuric acid.

When magnesium is likewise present in the mixed chlorides in any considerable quantity, this element should previously be removed with oxine as described on p. 71.

DETERMINATION OF BERYLLIUM. GENERAL CONSIDERATIONS.

Beryllium is a constituent of highly sodic acid rocks and more than traces have often been detected in these. The determination of this element becomes only a matter of importance in the analysis of definite beryllium minerals and it is likely to become a more common constituent of light alloys. The determination can be carried out in the ammonia precipitate after separation of the other elements by means of oxine or tannine, or preferably, after a preliminary separation, from aluminium alone by the same reagents. The non-determination affects the percentage of aluminium, unless when the ammonia precipitate is fused with sodium carbonate, then beryllium accompanies iron. [85)]

According to SCHOELLER and WEBB [85a)] fusion with sodium carbonate provides a rather satisfactory method for the separation of beryllium from other elements such as phosphorus, aluminium, chromium, etc. Beryllium remains nearly quantitatively in the residue of an aqueous extraction. The determination of beryllium in solutions containing sulphates should be avoided, as even double precipitations are insufficient to remove all the sulphate from the precipitate. Nitrate and chloride solutions are entirely satisfactory.

DETERMINATION OF BERYLLIUM AFTER SEPARATION OF ALUMINIUM WITH OXINE. PROCEDURE.

When beryllium is to be determined, [86)] the ammonia precipitate is separated as described on p. 47 seq.. Aluminium, phosphorus and beryllium are finally obtained in feebly acid solution. Aluminium is precipitated by means of oxine. [87)] Not more than 0.08 g Al_2O_3 should be present. So, with rocks, an aliquot portion (generally half the volume) must be used; with beryllium minerals, the whole volume may be taken in most cases. The solution is diluted to 300 ml and warmed to 50—60°. Then, 2 % oxine-ammonium acetate solution is added in 20 % excess over the required amount. A concentrated solution of 80 g ammonium

acetate in water is added and the liquid is allowed to cool with occasional stirring. The precipitate is collected with the aid of a glass filter crucible, washed with hot water and dried at 110—140° for at least one hour. Factor for Al_2O_3 : 0.1110.
for Al : 0.0587.

Aluminium may also be determined titrimetrically with bromate standard solution.

The *filtrate* is heated near to boiling point and ammonia is added in the same careful way as has been described in former sections, otherwise some beryllia may re-dissolve. The precipitate adsorbs some oxine and will therefore not be white, but this is without consequence. Dissolve the precipitate in dilute HCl and re-precipitate as before. Some macerated filter paper can be added with advantage. The precipitate is collected on a filter with small pores, washed thoroughly with a hot 2 % solution of acetic acid, just neutralized with ammonia. The filter is transferred moist to a weighed platinum crucible and is ignited, finally with the aid of a Meker burner or blast. The precipitate is extremely hygroscopic; so, the crucible should be cooled in a dessicator over phosphorus pentoxide and the constancy of weight should be ascertained. The precipitate should be tested spectrographically for contamination and at least phosphorus should be determined if there is any possibility of this element vitiating the results. This can be done in the ordinary way after a fusion with sodium carbonate.

As an alternative, beryllium may be estimated by hydrolisis with ammonium nitrite and as phosphate [88]).

DETERMINATION OF BORON. GENERAL CONSIDERATIONS.

Qualitative tests for boron are rather unsatisfactory for small percentages of this element in silicates. In boron *minerals* it can always be detected by fusing the powder with acid potassium sulphate and finely powdered fluorspar in a loop of platinum wire in the flame of a Bunsen burner. In rocks it is found as a constituent of certain minerals, such as tourmaline, dumortierite, and its detection is consequently most conveniently made by the inspection of slides with a polarising microscope. These minerals contain about 10 % of B_2O_3.

The quantitative determination of boron is by no means an easy task. The presence of boron interferes in several stages of an ordinary silicate analysis, viz. in the determination of silica,

where it is co-precipitated and volatilized in the hydrofluoric acid treatment, causing high values for silica, and in the determination of the sesquioxides, where it cannot be removed, even by three subsequent precipitations, thus causing high values for aluminium. Small amounts of boron are not caught quantitatively in these precipitates, nor in those of calcium and magnesium and this will make the sum of the analysis low. For all these reasons, boron should be removed prior to the separation of silica by volatilizing it as methyl ester. In the alkali determination after decomposition by the LAWRENCE SMITH method very small amounts of borax may contaminate the weighed alkali chlorides, most of the metal separates as calcium borate in the cake and in the subsequent treatment. Boron is expelled in an attack with hydrofluoric (and sulphuric) acid without particular precautions and will not cause difficulties in subsequent operations. After decompositions with fused carbonates, part of the boron is volatilized in the evaporation with hydrochloric acid. The remaining part should be removed by repeated evaporations of the dry salts with 30 ml portions of methyl alcohol saturated with gaseous hydrochloric acid.

A separate portion of the sample is used for the determination of this element by the volatilization method [89]: a separation of boron from all other elements is carried out by distilling off the former as the methyl borate ester. The distillate may be titrated or taken up in an aqueous solution of calcium hydroxide. In the latter case, the amount of boron will be found after ignition as the increase in weight. The titrimetric determination is more accurate and less tedious to carry out than the gravimetric procedure.

As pointed out by VAN NIEUWENBURG [24], boron minerals are often incompletely attacked by carbonate melts and much better by fused potassium or sodium hydroxide. [90]

DETERMINATION OF BORON. PROCEDURE.

Attention should be paid to the chemical composition of the glass apparatus in which the analysis is carried out, as most resistance-glasses contain considerable quantities of boron. Though these glasses resist fairly well the action of the liquids used in the analysis, this care will not, however, be superfluous, as boron-minerals and rocks which contain boron are likely to contain fluorine and attack of the glass is to be feared, due to

the action of the fluorine-compounds. It is always safe to carry out the necessary operations in platinum, silica or boron-free glass apparatus.

A portion of not more than 0.5 g of the sample neither con-

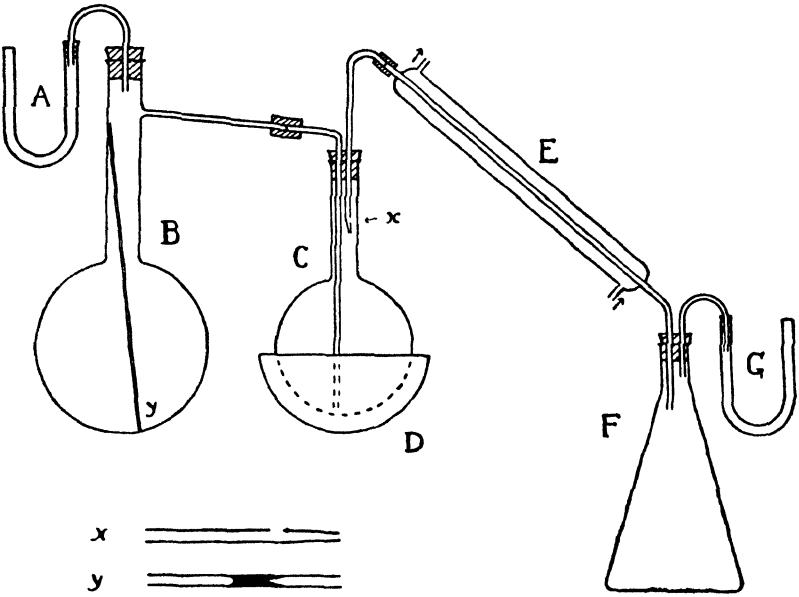

Fig. 8. Apparatus for the determination of boron.

1. A. Safety tube to avoid a too high pressure in the system; contains a little mercury.
   B. 500 ml distillation flask for methyl alcohol, supplied with a capillary "boiling tube". made from 3 mm glass tubing, closed at 1 cm from the lower end; represented on a larger scale as "y".
   C. 250 ml distillation flask, placed in a porcelain dish (D) filled with
   D. water. Make sure that the flask is surrounded by water and does not touch the dish. The end of the rather wide outlet tube is separately given as "x". This is an effective way to allow a free passage for the vapours in the tube.
   E. Glass condenser, length 40 cm.
   F. Receiving flask of 250 ml capacity.
   G. Safety tube, contains a few ml water.
2. A duplicate apparatus is required, beginning with C (provided with boiling tube and one hole stopper in this case). The whole flask can be heated in a steam bath. Condenser and receiver as in 1, E and F, but without G.
3. A suction pump is required to reduce the pressure in the second distilling apparatus. A three way cock permits to restore the atmospheric pressure in 2.

taining more than 0.1 g of B_2O_3 is fused with sodium potassium carbonate in equimolecular mixture. It is important, not to heat the sample in this operation at higher temperatures than are strictly necessary to achieve complete decomposition, otherwise some boron may volatilize already. The detached melt is transferred to a 250 ml distillation flask and *just enough* hydrocloric acid, 1 : 1, is added to neutralize the carbonates. This operation need not be hastened, the flask being placed up to the neck in cold water to prevent escape of the boron by volatilization with water vapour. For every ml of solution in the flask, about 1 g of anhydrous calcium chloride is added, to serve as a dehydrating agent. Pure anhydrous methyl alcohol is distilled into the liquid after the apparatus of fig. 8 has been fitted up. After 25 ml have condensed, the dish with water is heated with a small flame and the temperature is so regulated that the total volume remains constant in the flask. About 100 ml of distillate are collected in this way, after which a new receiver is attached to the apparatus. The water in the U-tube is added to the solution in the flask and the liquid is titrated with standard sodium hydroxide solution first with a few drops of a 1 % paranitrophenol solution as indicator and then on phenolphthaleine (1 ml). For small amounts of boron, a 0.1 N solution is used for the titration, for larger quantities 0.5 N will be more suitable to keep the volume of water low. A quantity of sodium hydroxide, equivalent to twice the amount added between the two end-points, is added to the liquid and in the second distillation apparatus, the alcohol is boiled off. The second 100 ml distillate is treated in the same way and should not require more than 1 ml of 0.1 N sodium hydroxide solution after which the distillation may be considered to be complete; otherwise the operation should be repeated, using more calcium chloride to arrive at a better dehydratation.

After most of the alcohol has been expelled from the solution, the latter is rinsed with two small portions of water in a porcelain dish and heated over a low flame to remove traces of alcohol still remaining. The residue should now have a volume of about 25 ml, if less, water is added to this amount. Subsequently the solution is returned to the flask and exactly neutralized on both indicators with 1 : 1 hydrochloric acid, avoiding any excess. After slightly heating the solution on a warm waterbath, the flask is supplied with a boiling tube and connected with

the suction pump and the liquid will soon begin to boil owing to the reduced pressure. When cold, the carbon dioxide will have been removed. The solution is now neutralized with 0.5 N sodium hydroxide to combine with the amount of less than one drop of hydrochloric acid, 1 : 1, present in excess; the procedure is repeated alternating with 0.1 N HCl and 0.1 N NaOH. In both cases, one drop should restore or cause the disappearance of the colour of the paranitrophenol.

After the addition of 1 g of mannite or 50 ml of pure neutral glycerine, the solution is titrated with standard sodium hydroxide solution until the end-point with phenolphahaleine is reached.[91]) The strength of the standard solution should be ascertained by titration of an approximately 0.1 N solution of anhydrous boric acid and the results should be corrected for those on a blank with the reagents alone. HILLEBRAND, on the authority of PENFIELD, FOOTE, SARGENT and FORD moreover recommends repeating the operation (viz. fusion after ignition, and carrying through the method) on the residue in the decomposition flask after filtration.[92]) cf. [90])

DETERMINATION OF FLUORINE. GENERAL CONSIDERATIONS.

Fluorine is found in igneous rocks of all kinds and especially in the highly acid rocks such as granites and pegmatites, but it occurs also in basic rocks as a constituent of most apatites. If fluorine bearing minerals other than apatite are absent, 6—10 % of the percentage of P_2O_5 may be considered to be the percentage of F in the rock, but this rough indication will only give the order of magnitude. The presence of fluorine affects the accuracy of the silica-determination, but the effect is very small in ordinary analyses as theoretically not more silica than 0.77 of the total amount of fluorine can be lost as silicon tetrafluoride and the loss is generally much less owing to the volatilization of hydrofluoric acid alone in aqueous solutions. On the decomposition of fluorine-bearing minerals by fused carbonates, the temperature of the melt should be kept low, to avoid loss of fluorine and silica. Sometimes it will be necessary to add pure silica to combine with the fluorine, but this is not required, unless the percentage of silica is substantially lower than that of fluorine. The determination of fluorine in small amounts has been very improved by the colorimetric procedure of STEIGER,

making use of the decrease in intensity of pertitanate solutions on the addition of soluble fluorine compounds. The old method of BERZELIUS for the quantitative determination of both fluorine and silica has been modified to a less tedious and indeed fairly satisfactory procedure by HOFFMAN and LUNDELL and the weighing of fluorine as lead chlorofluoride is preferable to the calcium fluoride method.

a. COLORIMETRIC DETERMINATION OF FLUORINE. PROCEDURE OF STEIGER.

As this procedure [93]) will yield a satisfactory determination only for relatively small amounts of fluorine, it is well to take a 2 g portion of the sample and to fuse this with four times the

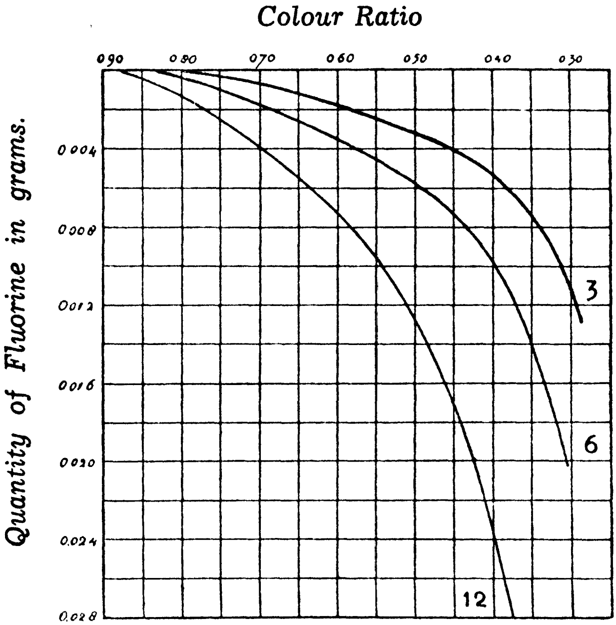

Fig. 9. Colorimetric determination of fluorine. Merwin's diagram for Steiger's method.

The colour ratio may be defined as the proportion:

$$\frac{\text{apparent amount of titanium in the test solution}}{\text{amount of titanium present in the standard solution}}$$

Valid for temperatures between 19—25°, when both solutions have the same temperature.

amount of sodium potassium carbonate, or with 7 g sodium carbonate. The cake is leached with water. To remove the silica, aluminium, iron and other interfering elements, about 4 g of finely powdered ammonium carbonate are added and the liquid is heated on the waterbath to destroy the excess of the precipitant, as this would likewise have a bleaching effect in the colorimetric procedure. To the filtrate not larger than 75 ml by volume are added 0.01 g of TiO_2 (as standard solution), and a few ml of hydrogen peroxide. The solution is neutralized by adding concentrated sulphuric acid. The total volume should not be more than about 90 ml, to be able to make it up to just 100 ml. After neutrality has been reached, the addition of one more drop of sulphuric acid causes the appearance of a light yellow colour, disappearing on the alternate addition of a few drops of sodium carbonate solution. To the neutral liquid are added 3 additional ml of concentrated sulphuric acid, the solution is made up to 100 ml and is compared with a solution also made up to 100 ml and containing besides 0.01 g of titanium, an equal amount of hydrogen peroxide and of sulphuric acid as the test solution. The "colour ratio" of both solutions is compared and the result is plotted in Merwin's diagram (fig. 9). If, owing to the concentration of fluorine, a point of the steep part of the curve for 3 ml is cut, (to the right of colour ratio 0.40) add 3 ml of concentrated sulphuric acid to the *test* solution, stir vigorously and again determine the colour ratio and, if necessary, once again after the addition of further 6 ml of sulphuric acid. For larger amounts than 20 mg of fluorine the procedure is inaccurate and a gravimetric determination is required. In the case that only 50 ml of the solutions are compared in the colorimeter, only half the amounts of sulphuric acid will be subsequently added. This corresponds to percentages up to 1—2 % of fluorine, according to the weight of the portion.

b. GRAVIMETRIC PROCEDURE. [94]

An amount of the sample corresponding to 0.01—0.1 g. of fluorine — ordinarily weighing 0.5 g for most minerals, and for rocks containing percentages of fluorine which cannot be estimated colorimetrically, — is fused with 5 g of the fusion mixture

of carbonates, the cooled melt is leached with hot water and the solution is filtered off after complete disintegration. The residue is extracted in a dish with 50 ml of a boiling 2 % solution of sodium carbonate. After this operation the solution with the remaining traces of fluorine is filtered into the first filtrate, while the residue is reserved for the silica determination. To the combined filtrates (about 300 ml) is added 1 g of zinc oxide dissolved in 20 ml dilute nitric acid, 1 : 9 by volume. After boiling for one minute the residue is filtered off washed thoroughly with hot water and likewise reserved for the silica determination. The filtrate is coloured with a few drops of methyl red solution, *nearly* neutralized with nitric acid and evaporated down to a volume of less than 200 ml, care being taken, to avoid the solution becoming acid, as this would involve loss of fluorine. After the solution is cooled, it is acidified slightly with a few drops of nitric acid and is treated with 1 g of zinc oxide, dissolved in ammonium hydroxide with the aid of ammonium carbonate, (2 g of ammonium carbonate dissolved in 20 ml water and 2 ml concentrated ammonia). This solution is boiled in a covered platinum or fused silica dish — if one of platinum is not available — until the odour of ammonia is no longer perceptible, the volume of the solution will now be about 50 ml. The liquid is diluted with 50 ml of hot water, stirred, allowed to settle a few minutes and is then filtered from the residue. The latter is added to the former residues after thorough washing with cold water and will serve for the silica determination. In the filtrate fluorine is determined as follows:

To the neutral solution an indicator is added to allow of precipitation within the pH-range of 3.6—5.6. Bromphenol-blue, Congo-red and methyl-red are all suitable. Aluminium (even 0.5 mg), boron ($>$ 0.05 g), ammonium ($>$ 0.5 g) and large amounts of sodium or potassium (in total $>$ 10 g) interfere in this determination. If a gravimetric determination is intended, the chemist should make sure that phosphates, sulphates and carbon dioxide are absent, lest these be co-precipitated: less than 10 mg of these substances is said to be unobjectionable.

Two drops of the indicator are added to the neutral solution and 3 ml of a 10 % NaCl solution; the mixture is diluted to 250 ml, acidified with nitric acid and again made only just alkaline. 1 ml of concentrated hydrochloric acid is added and 5 g of lead nitrate, after which the solution is heated on the

water-bath to shorten the period of solution of the solid matter. As soon as this is the case, 5 g of sodium acetate. 3aq are added. After stirring vigorously, the liquid is digested for half an hour on the water-bath, with occasional stirring. After standing overnight at room temperature, the liquid is cooled under the tap or in ice water, filtered through a filter crucible with sintered glass layer and washed with a cold saturated solution of the precipitate and finally with a few ml. of cold water. Factor for F_2 after drying at 120—150° : 0.0726.

The washed precipitate can be titrated when the influence of interfering substances will be much less. After a filtration through paper, it is transferred in this case to the beaker in which the precipitation has been carried out and the whole is stirred until the paper is disintegrated to pulp. The precipitate is dissolved at the temperature of the water-bath, a slight excess of silver nitrate solution is added and after heating for another half hour, the solution is allowed to cool, the residue is filtered off, washed with cold water and the excess of silver nitrate is titrated back with standard ammonium thiocyanate solution. 1 ml of 0.1 N $AgNO_3$ solution is equivalent to 1.90 mg of fluorine.

Silica is determined almost in the ordinary way. The reserved residues are rinsed with a jet of dilute hydrochloric acid, 1 : 20, into the beaker used in the last precipitation. The ash of the ignited papers is added likewise and the contents of the beaker are digerated with 25 ml of concentrated hydrochloric acid. Silica is determined by double evaporation with intermediate filtration. The second evaporation, however, is carried out by heating until fumes appear after the addition of 10 ml of sulphuric acid to effect the complete dehydratation of the zinc salts. The small amount of silica which remains in solution can be recovered in an ammonia precipitate after the addition of 40 mg of aluminium as chloride, but this refinement will hardly be necessary.

The other constituents of the sample are best determined in a separate portion after attack with hydrofluoric and sulphuric acids — when necessary after a sodium carbonate fusion. Great care should be taken to secure the complete expulsion of any fluorine, as this element interferes in the determination of aluminium as well as that of calcium. Repeated evaporations until fumes of sulphuric acid appear, are necessary.

Fluorine displaces oxygen in the composition. As $2F^-$ are

equivalent to O^{2-}, the sum of the analysis will be too high. Therefore, subtract 8/19 = 0,42 of the percentage of fluorine from the sum.

DETERMINATION OF CHLORINE. GENERAL CONSIDERATIONS.

In igneous rocks, chlorine seems to be more or less exclusively found in highly sodic types, generally as a constituent of the sodalite "molecule". Some apatites contain chlorine in small amounts. Chlorine does not interfere with the determination of other elements, except that a correction should be applied to the oxygen content of the sample. 1 % of chlorine is equivalent to 0.225 % of oxygen. Consequently, if the determination of this element is omitted, the sum will be too low by 0.775 or about ¾ of the amount of chlorine present in the sample, if the metal with which it is combined is reported as the oxide.

Most minerals containing chlorine are easily soluble even in dilute acids. If this case holds, the finely powdered sample is extracted with very dilute chlorine-free nitric acid, 1 : 20. One gram of the sample is taken and 100 ml of liquid. Silicates insoluble in nitric acid alone are treated with a very dilute mixture of nitric and hydrofluoric acids. No chlorine is lost at all in these operations, as 0.1 N solutions of hydrochloric acid can be boiled without changing their titer, provided the evaporated water is replaced, or an appropriate reflux condenser is used. If the minerals which contain chloride are not wholely decomposed by any of the above treatments the analyst may have recourse to a sodium carbonate fusion. The chlorine-ion is determined, either gravimetrically, by weighing the silver chloride precipitated on the addition of a sufficient amount of silver nitrate, or titrimetrically.

DETERMINATION OF CHLORINE. PROCEDURE.

1 g of the sample is treated either with 100 ml of dilute nitric acid, boiling if need be, for a few minutes, or with a mixture of nitric and hydrofluoric acids, likewise very dilute. Or a fusion is applied with six times the weight of sodium and potassium carbonate mixture (free from chlorine) followed by an aqueous extraction of the melt. This extract is acidified with nitric acid.

In the filtered solution chlorine is precipitated by a slight excess of silver nitrate solution. The silver chloride is best collected in a filter crucible and weighed after it has been dried at a temperature not over 130°. Factor for chlorine 0.25, or for much chlorine 0.246. If need be, the precipitate can be dissolved in dilute ammonia and re-precipitated after filtration by the addition of nitric acid. This will be especially necessary, if the filtrate obtained after the decomposition is turbid through fine mineral particles or silica.

DETERMINATION OF SULPHUR TRIOXIDE. GENERAL CONSIDERATIONS.

In rocks and minerals, sulphur habitually occurs in the sulphide condition, but is sometimes found as sulphate in some complex silicates, e.g. hauynite and noselite. These are generally related to alkali rocks. Minerals of this group are soluble even in dilute acids. Commence the decomposition at a low temperature, cf. p. 40 and 43). To prevent sulphides being oxidized and attacked, decompose in an atmosphere of carbon dioxide.

DETERMINATION OF SULPHUR TRIOXIDE. PROCEDURE.

Approximately 1 g of the sample is weighed out and allowed to stand for two hours with 50 ml dilute hydrochloric acid, 1 : 5. After boiling for 15', the liquid is filtered off; residue and filter are thoroughly washed and the volume should be brought up to at least 200 ml, otherwise silica is likely to be precipitated after long standing. The sulphate ion is precipitated as described in the section on total sulphur etc. The barium sulphate is filtered off, washed thoroughly with hot water, ignited and weighed. For larger amounts, the sulphate may be purified by fusion with carbonate, aqueous extraction of the cake and re-precipitation with barium chloride. Generally in this case it will be better to remove the silica prior to the precipitation of barium sulphate as follows:

After treatment with acid, the filtrate is evaporated and silica removed as described on p. 44, seq. Then proceed with the determination of sulphate as described above. In case the whole sample is decomposed by this treatment (acid soluble silicates) and sulphides are absent, it is advisible first to decompose it with dilute hydrochloric acid and proceed with the separation of silica

without preliminary filtration, thus obtaining control for the percentage of SiO_2.

Factor for SO_3 : 0,34286.

ANALYSIS OF SOILS. GENERAL CONSIDERATIONS.

With regard to the analysis of soils only few general rules can be laid down. Ordinarily the methods of silicate analysis will be applicable without change. [95])

Large amounts of manganese and sometimes titanium may be expected and in this case, these elements should be separated and determined by gravimetric procedures. Manganese is frequently present in soils in the form of the peroxide and consequently interferes with the determination of carbon dioxide if hydrochloric acid is used in the decomposition of the sample. Sulphuric or phosphoric acid should be used instead. DIXON's method deserves special mention in this section as humus compounds and other organic matter are almost invariably found in soils.

Most of the humus present in soil samples can be oxidized by repeated evaporations with concentrated hydrogen peroxide. (30 %). So the total content of organic matter may conveniently, though approximately be determined according to this method by drying a weighed portion of the sample at well defined conditions before and after the treatment with H_2O_2. The pure reagent should be used and the insoluble parts determined by a blank. The loss in weight represents organic matter. I have found this method to be satisfactory in a number of soils and synthetic mixtures.

As, genetically, soils are intermediate products between igneous and metamorphic rocks on the one side, and sediments on the other, methods described for these materials are also worth while consideration in soil analysis.

Special procedures have been devised and have found much application in the partial analysis of soils for practical purposes; viz. extraction with very dilute mineral acids, with weak organic acids or even with water, to estimate manurial requirements etc.; further, repeated extractions with acids, gradually increasing in strength with alternate washings with sodium carbonate or caustic alkalies, in order to determine the mineral composition of the soil. These latter procedures have serious disadvantages

and are unsuitable for scientific work. The mineralogical composition should be determined by pure mineralogical and X-ray methods.

SEDIMENTARY ROCKS. GENERAL CONSIDERATIONS.

A description has been given of a rather complete course of analysis for igneous rocks and silicate minerals. The changes in the procedure to make it suitable for the analysis of other rock-types will be considered here and briefly described.

The phenomenon of weathering causes the physical and chemical disintegration of the primary igneous rocks, both leading to the formation of soils and new rock species *sediments.*

Some sedimentary rocks are rather similar in composition to igneous rocks; they are products, *mainly of physical disintegration,* or of *direct sedimentation of loose volcanic matter:* tuffs. Their analysis may be performed in accordance with the general course. Other sediments, however, the products of chemical actions, are of altogether different nature and require special procedures. They can be grouped under the following heads:

1. quartz-sands
2. clay matter; kaolin.
3. iron hydroxides (laterites)
4. aluminium hydroxides (bauxites)
5. carbonates
6. salt-deposits.

It is obvious that combinations of two or more of these groups are not rare. Then a compromise has to be made, or the ordinary course of analysis may be followed, which indeed is always applicable.

The different types of sedimentary rocks will be considered here:

QUARTZ-SANDS AND QUARTZITES, QUARTZ, CHALCEDONY AND OPAL.

The following abbreviation of the ordinary course of analysis may give satisfactory results and will save considerable time if the constituents other than silica are present only in very small amounts and if elements yielding sulphates undecomposable by heat (especially alkalies and alkaline earths) are either absent or their amount will be determined so that a correction can be applied.

The loss on ignition of a weighed portion of the sample of about 1 g is determined and if the above conditions are fulfilled this may be reported as *total water*. Next, the ignited sample is treated as if it were the separated silica of the main portion. The evaporation with 40 % HF should be repeated until no more undecomposed mineral fragments remain and this may last considerably longer here, than with the finely divided precipitated silica as quartz especially tenaciously resists the action of hydrofluoric acid. Finally, the contents of the crucible are moistened with a few more drops of sulphuric acid to expel all the HF and after this has been driven out, the sulphates are heated to secure the thermal decomposition of iron and aluminium sulphates. If the ignition has not been unduly prolonged nor the temperature raised too much (600—800° will be sufficient), a correction may be applied for the gain in weight resulting from the sulphate radicle. The loss in weight by the treatment with HF represents the *total silica* in the sample. This can be checked by a determination, either of silica in the ordinary way in a small portion, or by determining the silica indirectly as : 100 % — (loss on ignition + other constituents). [95a)]

KAOLIN.

Kaolin, ($2SiO_2.Al_2O_3.2H_2O$), is insoluble in mineral acids, except in hot, concentrated sulphuric acid. By heating the substance to a dull red heat (about 500°) decomposition takes place; [96)] amorphous silica and aluminium oxide are formed, the latter being easily soluble in most mineral acids. At higher temperatures, the aluminium oxide recrystallizes and becomes resistant to attack; at 900° this will be so almost instantaneous. Either of these procedures may be used, to keep the amount of alkali salts in the analysis low. The silica is separated by these treatments and is filtered off. It may be useful, to repeat the evaporation as has been described under silica, p. 44, seq. This silica, however, contains not only the common impurities, but also the minerals of the sample that are not decomposed by the described treatment. If the latter amount is small (cf. under 1; quartz-sands etc.) the described treatment will be quite satisfactory viz.: ignition of silica, followed by evaporation with HF. Otherwise it will be advisable to fuse this precipitate with the required amount of

sodium carbonate to purify the silica. As this procedure will probably give a not at all negligible amount of alkalies it will be simpler to apply sodium carbonate fusion directly. For rather pure clay substances the acid treatment is a very convenient one. In either of the described procedures, organic matter — which is not unlikely to occur here, now and then — will have been destroyed before it interferes with the precipitation with ammonia. It should be borne in mind that organic matter, as well as fluorine should be *completely* expelled before the precipitation of the sesquioxides is attempted. If organic matter is present, the carbon may be conveniently determined in the same sample as carbon dioxide according to the procedure described by DIXON. (p. 130, under carbonate rocks).

LATERITES AND BAUXITES.

These groups are treated together, as a sediment composed exclusively of only one of the two oxides will rarely be found. The main constituents are iron and aluminium oxides and hydroxides. Titania is always present, sometimes in large amounts and phosphorus also is a common constituent. Sediments of this type often contain considerable amounts of quartz.

If the percentage of unweathered minerals is high, the ordinary course of silicate analysis should be followed. This is indeed always the safe way, but other methods of attack have been described and, as their authors claim that these have considerable advantages, they will also be mentioned here.

Other fluxes that have been recommended are borax, pyrosulphates and alkali peroxides and hydroxides. A draw-back of borax is that the boron should be removed after the fusion as it will interfere with the determination of silica as well as in that of the sesquioxides. Methods of wet attack make use of sulphuric acid, either alone or in combination with hydrofluoric and nitric acids, with or without preliminary thermal treatment of the sample. [97]) Care should be exercised, not to heat the sample to higher temperatures than 550° (dull red heat) as this tends to make the aluminium oxide more resistant to acid attack, owing to the formation of α-Al_2O_3. The residue of a wet attack ought to be small and nearly white and will contain only negligible amounts of aluminium and titanium oxides, and possibly quartz,

if hydrofluoric acid has not been used. In the latter case, it should be treated with hydrofluoric acid to determine its silica content and otherwise, or after this treatment, the residue is fused with pyrosulphate and the sulphuric acid solution of the fusion cake added to the main portion.

For all these methods the use of a finer sample will shorten the time needed for the decomposition. Therefore, 5 g of the sample should be ground very fine in an agate mortar, preferably under alcohol or ether to prevent loss of brittle parts like quartz etc. 1 g portions of the orirginal and those of the extra fine sample are dried at a temperature of 105—110° in an oven. One is thereby enabled to recalculate the results after the completion of the analysis, on the basis of the original water content, as the extra fine sample generally contains much more hygroscopic water than the original sample.

After the determination of H_2O^-, the loss on ignition is ascertained with the same sample. This represents total water, carbon dioxide — if present — and organic matter. Ferrous iron and other, not wholely oxidized, constituents are not likely to occur and so, a further discrimination in this group will be possible after the determination of carbon dioxide and organic matter using the wet method of attack described on p. 130, seq.

The attack with sulphuric acid alone is carried out with 1—2 g of the finely divided sample. This is weighed out in the platinum basin and according to the amount of sample, from 25—50 ml sulphuric acid, 1 : 1, are added. The basin is placed over a very low flame or on a radiator, and the liquid is slowly evaporated until fumes of sulphuric acid are liberated, the heat being adjusted so as to make the operation proceed slowly for 4—6 hours, less or more time being needed in some cases. The residue is filtered off after dilution of the acid after cooling. The residue is ignited, weighed and treated with one drop of sulphuric acid and a few drops of hydrofluoric acid, to determine the silica in it. After this operation, the residue, which will now be very small, is fused with pyrosulphate and the melt is dissolved in the liquid obtained by the decomposition. This liquid should contain at least 10 % by volume of sulphuric acid, otherwise the titanium sulphate will probably hydrolize. The further treatment of the sample should be carried out according to one of the methods mentioned in the chapter on silicate rock analysis. For large amounts of titanium the gravimetric determination is the

only correct way and is best carried out after separation of the iron as sulphide in a solution containing enough tartaric acid to prevent the hydrolysis of aluminium and titanium compounds. The separation of titanium is subsequently carried out with cupferron.

Qualitative tests are made for calcium and magnesium in the filtrate of the ammonia precipitate or they are quantitatively determined if their amount is not negligible. Alkalies are almost always absent in sediments of this kind.

CARBONATE ROCKS. GENERAL REMARKS.

The main constituents of limestones and other carbonate rocks are calcite and dolomite, ($CaMg(CO_3)_2$). As a result of isomorphous replacement, manganese and iron are also frequently encountered in carbonates. Contaminations by sedimentary matter belonging to other groups, except perhaps salts, is a common phenomenon. As a rule, these constituents, as well as others such as organic matter, pyrites, Mg-silicates, Ca-silicates and gypsum, remain undissolved if the decomposition is made with very dilute acids, which can only just attack the carbonates.

The choice of the methods of analysis depends largely upon the degree of purity of the sample, and — if the sample is not exclusively composed of carbonates — whether the so-called insoluble part is to be analysed separately.

CARBON DIOXIDE.

The determination of this constituent has been described under the methods of analysis for silicate rocks. A wet attack is preferable to combustion methods. Thus, generally the sample should be decomposed by acids and the carbon dioxide liberated, caught in an absorption train. In a number of samples, the loss on ignition represents the carbon dioxide to some degree of accuracy.

The heating of dolomitic limestones and dolomites should be very cautious at first to prevent loss by the violent decrepitation that sometimes takes place due to the easy thermal decomposition of dolomite.

Water and organic matter, however, are included, so a further discrimination will be possible after the gravimetric determination of these constituents. Bivalent iron and other substances which may change in weight also affect the result.

In as far as carbon and carbonaceous matter will frequently be encountered in carbonate rocks and indeed in other sediments also, it is convenient that the analyst has at his disposal a method of analysis for determining both forms of carbon in one sample. DIXON has recently described a method which fulfills these

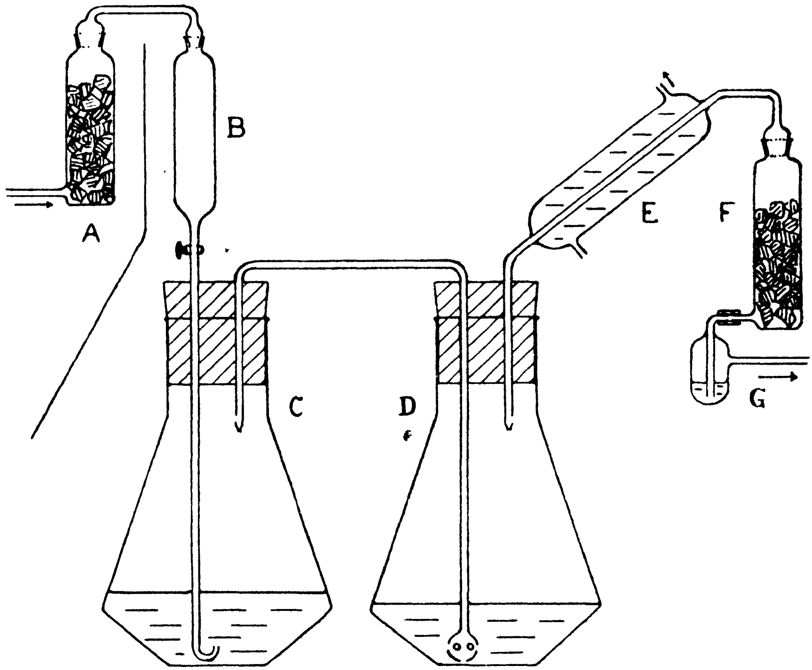

Fig. 10. Apparatus to determine carbon dioxide and carbon in one portion of the sample according to Dixon.

A. absorption-tube with soda lime to purify the air, sucked through the system.
B. Separatory funnel serving as inlet tube.
C. "Decantation flask" used for the decomposition of the sample.
D. Decantation flask acting as trap for incompletely oxidized vapours.
E. Reflux condenser.
F. Absorption tube containing pumice, impregnated with anhydrous copper sulphate to trap hydrogen sulphide.
G. To absorption train.

ıands.[98]) The carbon dioxide is expelled by syrupy phos-
ric acid and the gain in weight of the absorption tubes is
ırtained. Next chromic acid is introduced (a concentrated
.tion of potassium or sodium dichromate in phosphoric acid)
ı a little HgO as catalyst and the carbon or organic matter
oxidized by these agents. To trap any vapour which has not
ı thoroughly oxidized to carbon dioxide and water in the
ɔmposition flask, a second flask with a hot mixture of phos-
ric and chromic acid with a small quantity of mercuric oxide
ɗded to the train and the gases forced in fine bubbles through
liquid. The figure 10 will make clear the mode of construc-
of the apparatus. A permanent set up may most convenient-
ıe made which will serve equally well for the determination
arbon dioxide alone. The second flask should then be repla-
by a reflux condenser. The gain in weight of the absorption
ɜs represents the carbon dioxide, resulting from the oxida-
of organic carbon. For further particulars the original paper
ıld be consulted. The main advantages of this method are its
ɔlicity and the direct determination of the carbonaceous
ter in the same sample which has been used for the deter-
ation of carbon dioxide and which will be altogether free
ı this constituent. Consequently it is far superior to the ordi-
y method where total carbon is determined by combustion
hods and carbonaceous matter by difference.

'SOLUBLE PART. ANALYTICAL PROCEDURE.

he carbonates are decomposed as gently as possible by very
te hydrochloric acid, or if this is considered to attack the
oluble part" as well, acetic acid may be used. This operation
ıld be carried out after moistening the sample with a few
ɔs of water in a covered beaker or an inclined Erlemeyer
ɔo-called decantation flask fig. 10; the vertically projected
ɔlets of liquid will then not be lost. When the sample has a
ımitic character, heat will be necessary to attack the calcium
ɲesium carbonate. The operation is started with two por-
s, each weighing about 1 g. The insoluble residue is filtered
once with the aid of a small paper filter, the other time with
ɔrcelain or glass filter crucible. In the latter portion, the
ɜr content (H_2O—) of the insoluble matter — if important

at all — can be determined after weighing the insoluble part; the former portion serves to ascertain the loss on ignition. Therefore the filter is ignited moist, the residue is weighed and decomposed with a few drops of hydrofluoric acid and one of sulphuric acid to determine the silica (cf. quartzsand etc. p. 126.) The residue is generally composed mainly of sesquioxides and is preserved in the crucible to be added to any sesquioxides which may have gone into solution and will be found in the dissolved portion. If the residue is large, it had better be treated according to the usual methods of silicate analysis, or the composition of the bulk sample is determined as a whole by the ordinary methods.

SOLUBLE PART. ANALYTICAL PROCEDURE.

If much *silica* is considered to have gone into solution, its separation is necessary. The evaporation will take only little time as compared with the separation of silica after a carbonate fusion. The temperature should not exceed 120° in the case that magnesium is present, as it would combine with the silica to form a silicate, soluble in the subsequent operations. These are carried out in precisely the same manner as has been described fully in the foregoing part, except that for only small amounts one single evaporation will be sufficient.

When carbonaceous matter is present this should be destroyed if it is soluble in acid, to prevent the interfering action of these substances in the precipitation with ammonia. This is secured automatically in the treatment for simultaneous analysis of soluble and insoluble part, but when the soluble part is to be analyzed separately, it may be necessary to destroy the organic substances by heating the residue obtained by evaporation of the solution to temperatures at which the carbonaceous matter is decomposed entirely and burnt away. Sometimes a treatment with nitric acid or hydrogen peroxide will give satisfactory results and is then to be preferred for its simplicity.

The *precipitation with ammonia* should be carried out with a very pure carbonate-free reagent and with an adequate amount of ammonium chloride in the solution to prevent contamination with calcium and especially magnesium. If phosphorus is present in excess over the amounts of the other oxides, to be expected in this precipitate, a sufficient and known amount of some pure

iron compound should be added to combine with it. The required amount of hydrochloric acid is added to prevent co-precipitation of magnesium and after addition of a few drops of methyl orange, the precipitation is carried out in the same manner as has been described previously. Generally the separation of the mixed oxides is not necessary and after re-precipitation with ammonia, the filtered and washed hydroxides are ignited in the same crucible that has served already in the determination of the insoluble part. If need be, the separation may then be carried out with the combined sesquioxides of the insoluble and soluble part.

In the filtrate of the ammonium precipitate the *main constituents* are determined in exactly the same manner as has been described in the sections, *calcium* and *magnesium* in the foregoing part. The presence of manganese should be reckoned with. Further the analyst should take care that the concentration of magnesium does not surpass the limit of about 100 mg MgO/100 ml of liquid in the precipitation of calcium with oxalate. The separation of small amounts of calcium from large quantities of magnesium is a problem not frequently encountered in the analysis of sedimentary rocks. For the separation of the calcium as sulphate see under mineral analysis.

The separation of magnesium will be very slow in the presence of large amounts of ammonium salts. If a quick determination is called for, either the oxin-procedure should be adopted, or the ammonium salts should be removed by any of the well known procedures or the method described by SHEAD and HEINRICH may be employed. [98a])

The determination of the other constituents will not cause great difficulties.

Water escaping below 110° is determined in one of the portions taken for the decomposition with acid. Total water according to the PENFIELD method (Care being taken to heat dolomitic limestones very cautiously to prevent decrepitation). If larger amounts of sulphides are present, the water should be determined in a combustion furnace with a layer of lead oxides heated to 400° to prevent the interference of sulphur oxides.

The *alkalies* can be determined according to LAWRENCE SMITH. They are obviously entirely in the insoluble part. When calcium chloride is added as such, the lime of the carbonate rock will serve as flux, if ammonium chloride is added to yield calcium

chloride by double decomposition, an equivalent amount of pure calcium carbonate should be added as the coarsely crystalline limestone does not react easily with the sal-ammoniac vapours. The former procedure, however, is to be preferred.

Ferrous iron is largely present — if at all — in the soluble part as iron II-carbonate and may be titrated with permanganate solution after decomposing the sample with sulphuric acid. In the insoluble part, the ferrous iron is determined after the titration. Therefore this residue is filtered off (glass filter crucible), is rinsed quantitatively into a large platinum or palau crucible and decomposed as has been described in the section on ferrous iron.

In the presence of carbonaceous matter the determination of *ferrous iron* will generally be incorrect. If the organic compounds are insoluble in the acid used for the decomposition, they may be filtered off quickly and preferably in an atmosphere of carbon dioxide. The amounts of ferrous iron found are to be recalculated on trivalent oxide (Factor: 1.111) and the respective amounts of total iron in soluble and insoluble part are to be corrected for it.

The decomposition is carried out as follows: the sample in a narrowmouthed Erlemeyer flask is boiled with enough water to prevent excessive crusts of calcium sulphate covering the undecomposed carbonate. Dilute sulphuric acid is added in small portions at a time a new portion being supplied as soon as the effervescence ceases. The calcium sulphate will separate out and the iron goes into solution. When further addition of acid causes no more effervescence, the solution is cooled quickly by placing the flask in a basin with cold water and the liquid is titrated immediately, when still only warm, with permanganate solution. The oxidation by oxygen from the air is very slow in sulphuric acid solution without HF.

Phosphorus is determined in the soluble part after decomposition with nitric acid, in the insoluble part after fusing the latter with sodium carbonate in the ordinary way and when only total phosphorus is required in the combined liquids from these two decompositions.

Sulphur is determined after ignition of the sample either as such or after mixing with an equal amount of sulphate-free sodium carbonate, followed by extraction of the melt with water. Potassium nitrate need not be added if the amount of carbona-

ceous matter is not excessive as the sulphide sulphur is oxidized readily by oxygen from the air and the oxides are retained quantitatively by the lime. Very impure samples require more sodium carbonate for complete attack. Sulphur is determined in the solution as has been described on p. 103.

The state of the sulphur — generally sulphide sulphur — is ascertained by boiling a small amount of the sample with dilute hydrochloric acid. A lead acetate paper or the smell will indicate the presence of hydrogen sulphide in the escaping gases. The extraction of sulphate sulphur may be attempted in a carbon dioxide atmosphere with dilute hydrochloric acid, whereby pyrite is not attacked and the other sulphides decomposed without oxidation of the hydrogen sulphide.

When the insoluble residue is not to be analysed separately, the strongly decomposing action of quick lime may be used to attack the insoluble minerals. The very fine powder is heated for about 15' with a blast in a platinum crucible and becomes entirely soluble in dilute acids by this treatment provided the impurities do not exceed a certain limit, above which the addition of sodium carbonate becomes necessary. Proper care is required in the ignition of dolomitic samples to prevent loss by decrepitation. See p. 130. At the same time, the behaviour of the sample when heated is a valuable test for its general character; whether dolomitic or not.

According to HILLEBRAND, the behaviour of the sample under investigation should be tested on this point when the impurities exceed the limits of about 15 % for silica and 6 % for sesquioxides.

As carbonaceous matter is destroyed by this procedure, difficulties will not arise in the precipitation with ammonia. After the thermal treatment either with or without the aid of sodium carbonate the sample is dissolved in dilute hydrochloric acid after slaking the quick lime with a small amount of water. The separation of silica and other operations are the same as in the case that the soluble part is analysed.

SALT DEPOSITS.

The analysis of salt deposits will not be described here as the general course of their analysis is altogether different from that of silicate analysis. They will be taken into account on p. 151 in a separate chapter on the analysis of minerals.

METAMORPHIC ROCKS. GENERAL REMARKS.

Metamorphic rocks have their origin, either in igneous, or sedimentary rocks. Though the processes of metamorphism may effect local changes in chemical composition, the constituents as a whole — except perhaps carbon dioxide and water — remain in the bulk of the mass. Metamorphic rocks are consequently to be treated in the same way as the matter from which they originated.

ANALYSIS OF CEMENTS. GENERAL CONSIDERATIONS.

The term „cement" has a very extended application, but will be exclusively used here for the so-called hydraulical cements, in accordance with the general use. Their essential components are: lime, silica and aluminium oxide. Other compounds go into the composition, either replacing partly the above constituents (e.g. iron oxides instead of alumina), or as padding (e.g. slags; iron Portland cement), or merely as involuntary contaminations of the used materials. Limestones and marls are among the most common raw materials for the cement industry. Furthermore, furnace slags are used, 1 part of CaO being added to 4—5 parts of slag, or more complex mixtures are made. Marls used in the natural Portland cement industry, contain from 1.6—2.3 parts CaO to one part $SiO_2 + Al_2O_3 + Fe_2O_3$. The best Portland cements contain approx. 66 % CaO, 22 % SiO_2, 6.5 % Al_2O_3, 2.5 % Fe_2O_3, 1 % MgO, 1 % SO_3 and 1 % of several other constituents.

Cements are almost entirely soluble in dilute hydrochloric acid, without any preliminary decomposition. The insoluble part is filtered off, dried and weighed; its percentage is a *characteristic property*. Therefore, the sample should not be heated before the decomposition, as the insoluble part may become soluble in hydrochloric acid, owing to the strong action of the lime at higher temperatures; so, the loss on ignition is to be determined in a separate portion of the sample.

The methods of determination for the constituents are the same, as described in the sections on the analysis of these elements in silicates and especially in carbonate rocks. The alkalies are determined according to the L. SMITH method, but without

the addition of calcium carbonate, enough lime being present to decompose the insoluble part. 5—10 g cement are taken. This requires 0.5—1.0 g pure calcium carbonate, converted to chloride, to be added. See p. 134.

ANALYSIS OF SLAGS. GENERAL CONSIDERATIONS.

Furnace slags and slags resulting from other metallurgical operations have rather a variable composition. The limits for the most important constituents are indicated as follows:

SiO_2 : 20—65 %, Al_2O_3 : 1—22, FeO : 0—4, MnO : 0—5 *), MgO : 0—10,
CaO : 35—55, Na_2O : 0—3, K_2O : 0—2, H_2O : 0—4, TiO_2 : 0—2,
CO_2 : 0—3, P_2O_5 : 0—20, SO_3 : 0—1, (Ca, Mn) S : up to 6 %. [99]

In special cases, up to 3 % PbO, 20 % ZnO and even 50 % Cu_2O have been found in slags. Slags, especially when finely divided, are easily soluble in dilute acids, see p. 40 and 43.

The residue is fused with sodium carbonate, the melt dissolved in hydrochloric acid, carbon dioxide is boiled out and the liquid is added to the solution containing the soluble part.

Special provisions are required in the determination of silica when much lead is present. In this case, the decomposition as well as the dehydratation of silica should be carried out with perchloric acid. Lead and copper are precipitated with hydrogen sulphide, as described in the section on carbonate minerals and in the chapter on the analysis of ore minerals. The separation of zinc as the sulphide is carried out directly afterwards, as described in the section on the analysis of carbonates, p. 155.

It is advisable to make a qualitative search for these constituents to ascertain, if it is necessary to make these provisions. When lead separates with the silica, attack and damage of the platinum crucible is to be feared.

The further procedure for the analysis of slags is exactly the same as described for silicate rocks. The determination of ferrous iron may be impossible when metallic iron, or excessive amounts of sulphides are present. Metallic iron can be more or less completely removed with a magnet, but in this case, *combined* iron is largely present as FeO and may be stated as such.

Minor constituents (especially those, mentioned on p. 32—34.

*) up to 40 % in Bessemer slags.

as occurring in basic igneous rocks, viz. V, Cr, platinum metals, etc.) are best determined with spectroanalytical methods, or other special procedures.

ANALYSIS OF GLASSES. GENERAL REMARKS.

Every chemist should be able to determine accurately the constituents of the glass, used in the construction of apparatus required for carrying out analyses, as serious errors may be made in the determination of traces of many elements which occur in the very complex glasses manufactured to answer the demand for many purposes and properties.

Originally, glasses contained only few elements as intentional main components, viz. silica, calcium, sodium potassium. Unintentional constituents have always been present. To obtain glass-species with determined chemical, optical, thermal and still other physical properties, a large variety of elements are added to the raw materials in glass-manufacture, especially lead, barium, boron, zinc and antimony. To obtain colourless melts, manganese and cobalt compounds are introduced; other substances, either in colloidal or true solution and often in minimum amounts, yield glasses with beautiful colours. E.g. gold, cobalt, manganese and uranium serve for these purposes. To obtain clear, homogeneous melts, without gasbubbles, volatilizable substances are added like arsenic, ammonium compounds etc.; some of these are retained slightly in the melt. As the raw materials need not necessarily be very pure in all cases, the analysis of glass may become as complicated and even more difficult to carry out, than the analysis of rocks.

It is always advisable to test for several of the above mentioned constituents qualitatively, as their presence or absence may require or permit changes in the procedure of the analysis. Colour, "total appearance", refractive index and purpose for which the glass is intended, may give valuable information on this matter. Resistance-glasses often contain considerable quantities of zinc and boron. Zinc is not easily detected qualitatively, except by microchemical tests. Boron trioxide is detected by the green colour imparted to the colourless flame of a Bunsen burner, when a mixture of acid potassium sulphate with finely powdered fluorspar and the glass powder is heated in a loop of

platinum wire. Metals of the hydrogen sulphide group are qualitatively detected and quantitatively separated after decomposition with hydrofluoric and nitric or perchloric acids. Sulphur trioxide is detected and quantitatively determined in the acidified aqueous extract after a carbonate fusion. In every case, spectroanalytical analysis will be the most convenient way to make a qualitative analysis for rare constituents, otherwise large portions (up to 20 g and more) may be required for the detection and determination of small percentages of particular elements.

PROCEDURE OF GLASS ANALYSIS.

Analyses of *ordinary glasses,* made of pure raw materials, are relatively simple to carry out. After decomposition with 3—4 times the weight of sodium carbonate, the analysis of the main portion is carried out in the ordinary way. As an alternative for the alkali determination, the analyst may often with advantage use a hydrofluoric acid attack.

Borosilicate glasses are treated after the first evaporation for the silica determination, in the same way as boron minerals, (p. 114, seq.). Zinc is determined after the separation of the ammonia precipitate either by electrolytic methods (p. 227), or by precipitation with hydrogen sulphide after the addition of sufficient mercury II-chloride to ensure the quantitative precipitation of zinc, p. 64. In the determination of the alkalies according to LAWRENCE SMITH, some borate may be dissolved, so a treatment with methyl alcohol saturated with hydrogen chloride will be necessary, or a hydrofluoric acid attack (modified BERZELIUS method p. 146 and 193) will serve better as one gets rid of the boron at the beginning of the operations, in the decomposition, without further trouble. The boron content is determined as described in the chapter on mineral analysis, see p. 115.

Lead glasses are coloured dark black when fused in a reducing flame. The same holds for glasses, rich in antimony. In both cases the decomposition for the alkalies cannot be done in a platinum finger crucible. A specimen made of sheet iron or porcelain may serve here. In the main portion, the silica should be dehydrated with nitric or perchloric acid to prevent excessive precipitation of lead as chloride. Nevertheless, the silica should be washed carefully with hot water and the absence of lead in

the last filtrate should be ascertained. Great care should be taken throughout the whole analysis of these glasses, to prevent the deterioriation of platinum apparatus. In the fusion of the main portion, some nitre may be added; in the ignition of the silica the chemist should make sure of taking no risks.

After the separation of silica, a *nitric* acid solution is evaporated down thrice with hydrochloric acid to convert the nitrates to chlorides. On introducing hydrogen sulphide, the lead is precipitated as sulphide and weighed after filtration, convertion to lead sulphate and ignition. The filtrate is oxidized with bromine water at the boiling point and the further procedure is that of the ordinary course of analysis. The alkalies are determined after a hydrofluoric acid attack, followed by separation of all the other elements, lead in the first place as sulphide, according to one of the described procedures. p. 146 and 193.

Antimony and arsenic are likewise determined after a hydrofluoric acid attack. When barium is present, sulphuric acid should be avoided in the decompositions and nitric acid used in its place. The residue is dissolved in hydrochloric acid and hydrogen sulphide is passed into the liquid. Antimony is separated as sulpho-salt from lead. In other than strongly oxidizing attacks, trivalent arsenic escapes as volatile fluoride. Only quinquevalent arsenic is retained in ordinary attacks and will accompany the antimony. Trivalent arsenic is determined by difference. The percentages of both metals are generally so small as to obviate the necessity of applying a correction to the percentages of other constituents; moreover the contamination of precipitates will be unimportant in most cases, as arsenic and antimony are volatilized in several stages of the analysis before they can do harm.

Barium is determined, together with calcium, according to the sulphate procedure p. 153. Both metals are separated after converting them to carbonates by the chromate procedure. If only small amounts of calcium are present, the co-precipitation of this element in the determination of barium as sulphate is almost negligible and calcium may be separated as oxalate, afterwards.

Chlorine is determined after decomposition of a 5 g portion with a mixture of perchloric and hydrofluoric acids, both free from chlorine, in the presence of silver nitrate and heating until fumes of perchloric acid begin to escape. After the decomposi-

tion, the liquid is diluted with 400 ml of 1 % nitric acid and after standing overnight, the silver chloride is collected in a filter crucible.

ANALYSIS OF PLANT ASH. GENERAL CONSIDERATIONS.

A chapter on the above subject is included in this book, as the analyst, working on problems of geochemistry is likely to meet with a case, in which he will also have to make analyses of plant ashes and, as a rule, the relations between plant and soil make it necessary to investigate their properties with similar methods. [100])

There is a large variability in the chemical composition of plant ashes. This is a direct consequence of the conditions of the soil and the particularities of the food-supply for different plants. In general, it can be said that the ordinary chemical constituents of rocks and soils are present, but in altogether different percentages than in these. Aluminium, however, is entirely absent, whilst silica is not predominant here in most cases. Manganese is sometimes present in considerable amounts, up to 25 % Mn_3O_4. Potassium preponderates over sodium. P_2O_5 may represent about half the weight of the ash. Sulphur trioxide and chlorine are *essential* constituents. Carbon dioxide resulting from the incineration of organic matter often combines with an excess of bases and is not always expelled in the preparation of the ash.

See p. 2: biophile elements and Table V.

Thus, plant-ashes are composed mainly of phosphates, sulphates, chlorides and carbonates of the alkali and alkaline earth metals with — usually smaller — quantities of iron, manganese, and silicon oxides. In addition, a number of rarer constituents have been found in plant ashes : boron (up to 1 % B_2O_3), arsenic zinc, iodine and many others. As their occurrence is more or less accidental, general rules cannot be given for the necessity of looking for particular constituents. A spectrographic investigation will readily reveal the presence of every uncommon constituent with unrivalled precision. The behaviour of these minor constituents in physiological processes in plant life is not yet known for all cases. It is probable, that part of the fortuitious constituents are taken up more or less involuntarily during the growth of the plant, as a mass of water representing 300—400 times the weight of the dry matter is required, on an average,

for this process and, although a selective absorption by the roots seems to restrict somewhat the entry of non-biophile elements, these are not altogether excluded and subsequently concentrated in the ash.

PREPARATION OF THE SAMPLE.

It is advisable, to determine the *dry weight* of the matter, the ash of which is to be analysed, thus fixing a basis for the statement of the total ash content for reference purposes. The conventional procedure is the same as that which has been described for the determination of H_2O— in silicate analysis, i.e. drying at 105—110° in an oven. Unpublished experiments of the author ascertained the slow, but marked oxidation of organic substances at these temperatures. PROF. SCHOORL informed me that a better procedure is, drying the matter in vacuo at temperatures of about 80° over phosphorus pentoxide. Indeed no perceptible decomposition takes place and the results are reproducible, even in an atmosphere of air. As the dried plant parts are very hygroscopic, the operation should be carried out in weighing bottles and after heating, the thermal equilibrium with the surroundings must be established in a dessicator over phosphorus pentoxide. The dry-weight varies within about the limits 15—85 % of the gross weight.

PREPARATION OF THE ASH.

The ash for the analysis is prepared by carefully heating the sample in a platinum basin, or else a fused silica or a porcelain dish on a wire gauze over the *low* flame of a Bunsen burner. The organic matter should be carbonized at a low temperature to secure the easy burning of the resulting carbon and to prevent as much as possible, losses of S, Cl and K. Fusing or even sintering the ash should be avoided, as this will cause loss of volatile constituents and decrease the solubility of the ash in acids.

ANALYTICAL PROCEDURE.

The sometimes large amounts of phosphorus make it advisable to determine this element first, to be able to make provision for

it not interfering with the other parts of the analysis. If phosphorus is preponderant over the other oxides in the ammonia precipitate, calcium and magnesium will be co-precipitated and if these are *not* present, part of the phosphorus would remain in solution and separate at inconvenient times, or not at all.

For the determination of P_2O_5, the method described in the section on silicate analysis is to be preferred, i.e. expelling the silica of the sample by a treatment with hydrofluoric and nitric acids, followed by fusion with sodium or potassium carbonate. The melt is extracted with water and besides alkalies, only the sulphates of the sample and aluminium will accompany the phosphorus in the filtrate. Chlorine which would retard the precipitation of the phosphomolybdate is expelled during the decomposition by the repeated evaporations with nitric acid.

About 0.3 g of the ash are treated according to the instructions on p. 94, seq.; it should be borne in mind, that every 0.1 g P_2O_5 requires 3 g of the solid ammonium molybdate reagent. For the amounts usually found in plant ashes, the composition of the precipitate is too variable, for a single weighing of the latter to be sufficient to yield accurate results. Except when the procedure of VON LORENZ with sulphate molybdate reagent under special conditions is employed [124]), the precipitate should be dissolved in 10 % ammonia, and phosphorus reprecipitated in the filtered solution. Therefore the latter is acidified with hydrochloric acid, and to the boiling liquid, 10 ml of magnesia mixture are added for every 0.1 g P_2O_5. Next the solution is neutralized by adding dropwise 10 % ammonia. After 12 hours, a re-precipitation is carried out as has been described in the section on the determination of magnesium, but instead of the extra addition of phosphate, an additional ml of magnesia mixture is to be supplied here. The addition of ammonia to the boiling liquid should be done very gradually, as a surplus of acid phosphate in the liquid promotes the formation of the precipitate. After a few hours, the precipitate is filtered off, ignited and weighed as magnesium pyrophosphate. Factor for P_2O_5 : 0.63776;
for P : 0.27852.

The residue of the extraction of the melt, obtained in the sodium carbonate fusion serves to determine the iron content of the sample. This residue is dissolved on the filter in dilute hydrochloric acid and the iron is precipitated with ammonia in the filtrate. The precipitate is ignited and may be tested for

titanium, but as far as is known to me, this element has never been detected in plant ashes except in spectroscopic traces.

ANALYSIS OF THE MAIN PORTION.

In the main portion are to be determined: silica, (aluminium,) calcium and magnesium.

A 1 g portion of the ash is treated with dilute hydrochloric acid, 1 : 10, in a platinum basin or fused silica dish during one hour at the temperature of the water-bath. The residue is filtered off, ignited gently and weighed. The soluble part is conventionally reported as "pure ash".

The ignited residue is fused with 6 times its weight of sodium carbonate and the melt is dissolved in concentrated hydrochloric acid. The solution is added to the acid extract of the ash, silica is determined in the usual way. To the filtrate of the silica-determination, an exact known quantity of some pure iron salt is added, to make sure, that all the phosphorus is caught in the ammonia precipitate, without co-precipitation of alkaline earths. Thus, it will be safe to add an amount of iron, equivalent to that of the phosphorus. This precaution will be unnecessary only in case the phosphorus content is unusually low and enough iron is considered to be present. The iron compound should be specially free from aluminium if the determination of this element by chemical methods is planned. The precipitation with ammonia and the further treatment of the precipitate is carried out as has been described in the chapter on silicate analysis, but only the solution containing aluminium is examined. Aluminium — if present at all — is weighed as $AlPO_4$, an equivalent amount of phosphorus being co-precipitated. Factor for Al_2O_3 : 0.41788. For the small amounts of aluminium which will ordinarily be found — mere traces — it will scarcely be necessary to determine the phosphorus exactly after fusing the precipitate with sodium carbonate, followed by gravimetric determination of the phosphorus content of the precipitate.

In the filtrate from the ammonia precipitate, *calcium* and *magnesium* are determined in exactly the same way as in silicate rocks. *Manganese,* if present in large amounts, will contaminate the calcium oxalate as well as the magnesium ammonium phosphate and should be removed in this case previous to the determination of these metals. Ordinarily, the colorimetric estimation

in a separate portion and in the magnesium pyrophosphate will give satisfactory results but this should be ascertained in each particular case. *Water* and *carbon-dioxide* — if present at all — are determined in separate portions of the sample. *Chlorine* can be determined in the filtrate from an extraction with hot dilute nitric acid, both by titrimetric methods and by the gravimetric method, (p. 181). *Sulphate* is likewise determined in an acid extract of the ash. Hydrochloric acid should be taken for the decomposition and if large amounts of iron, (aluminium) and calcium are present, these are to be precipitated first with a mixture of ammonium hydroxide and ammonium carbonate. In the boiling filtrate from this precipitate, sulphate is precipitated with barium chloride solution after neutralization with hydrochloric acid and expulsion of the excess of carbon dioxide.

Sodium and *potassium* can be determined after decomposition of the ash with concentrated hydrochloric acid and separation of silica. In case the sample is not altogether decomposed by this treatment, a few ml of HF are added and the liquid is evaporated to fumes with a *small* excess of sulphuric acid. The residue from either method of decomposition is extracted with hot water in a platinum, fused silica or new porcelain dish. Pure, freshly prepared CaO is added until the reaction turns alkaline on phenolphthaleine; 200 mg CaO are added in excess and the liquid is gently boiled during 10'. The precipitate is filtered off and the filtrate, or an aliquot portion of it, is evaporated with 3 ml of 70 % $HClO_4$ in a small fused silica, porcelain or pyrex glass dish. *Potassium* is determined as described on p. 83. The filtrate from the potassium determination is diluted with water and evaporated after neutralization with pure MgO to lessen the chance of explosions, (p. 83). CaO and MgO are prepared, by heating the pure carbonates; the latter should be as free from alkalies, as required for the L. SMITH method.

Sodium, being present in plant ashes only in small amounts, is determined as triple acetate, based on the qualitative reaction discovered by Streng. [101]) Also, this method is advantageously applicable in other cases where minute amounts of sodium are to be determined. There is a recent, rather voluminous literature on this determination, but the most satisfactory procedure is that, described by KAHANE and by VAN KAMPEN and WESTENBERG; this is given here. [102])

The quantities of reagents indicated, are based on 1 ml of the

test solution. This should not contain more than 10 mg Na_2O (or 8 mg Na) or 25 mg K, (100 mg Rb or Cs). Ammonium, calcium, strontium, small quantities of barium, *magnesium,* iron, aluminium and chromium will not interfere. With regard to lithium, there is a controversy between the statements of KAHANE and KOLTHOFF; for plant ashes, however, the presence of lithium is quite out of the question.

The residue, obtained from the potassium determination is moistened with a few ml water. The liquid is filtered and the filtrate caught in a beaker, in which it is concentrated to approx. 2 ml. Sodium is precipitated by adding 15 ml of uranyl reagent. After standing *overnight,* the precipitate is filtered off by means of a filter crucible, washed five times, using 2 ml portions, with 96 % alcohol saturated with the precipitate and finally with a few drops of 96 % ethyl alcohol. Factor for Na_2O : 0.02022;
for Na : 0.01500.

For most ashes, owing to the higher percentages of sulphate, SMITH's method for the separation of the alkalies is not as suitable as for silicates.

After an acid decomposition, the alkalies also may be determined according to the principles given in the section on the analysis of natural waters, (p. 193). In this case, it is strongly recommended not to estimate sodium by difference, but to make a separate determination in the filtrate from the potassium chloroplatinate after reduction of the platinum compounds as described on p. 81—82. The accuracy of the indirect method (by difference) is too small for minute percentages of sodium, in the presence of much potassium. Even negative percentages of sodium have been found in unfavourable circumstances [103].

For *other constituents* and in the case that interfering substances are present in amounts, warranting their being taken into account, refer to the chapters on the analysis of rocks and minerals.

ANALYSIS OF COAL ASH. GENERAL CONSIDERATIONS.

As we have seen in the foregoing chapter, the composition of plant ash is ordinarily very different from that of silicate rocks. As fossil carbon is derived almost wholely from vegetable substances, one is apt to think, that the composition of coal ash will

CHARACTERISTIC ANALYSES OF PLANT AND COAL ASHES.

	1	2	3	4	5	6	7	8	9	10	11	12	
SiO_2	70.64	2.73	0.55	2.04	1.46	4.52	3.85	0—70	37.37	41.5	40—60	25—50	SiO_2
Al_2O_3	—	—	—	—	—	—	—	—	31.94	31.5	20—35	20—40	Al_2O_3
Fe_2O_3	1.42	1.42	0.29	1.10	0.51	3.35	1.41	0—10	19.74	18.4	5—25	0—30	Fe_2O_3
MnO	—	23.96*)	—	—	—	—	—	0—25	tr.	0.7	—	—	MnO
MgO	1.81	11.27	1.19	4.93	11.96	6.38	5.82	1—15	1.71	1.2	0.5—4	0.5—5	MgO
CaO	8.63	33.97	92.82	2.64	2.82	11.88	13.11	2—93	3.72	1.8	1—15	1—10	CaO
Na_2O	0.63	1.37	0.34	2.96	1.74	35.29	—	0—40	1.43	—	1—4	1—6	Na_2O
K_2O	8.01	19.66	4.36	60.06	30.51	16.56	43.19	0—60	0.13	—			K_2O
TiO_2	—	—	—	—	—	—	—	—	1.83	—	0.5—3	0—3	TiO_2
P_2O_5	1.37	2.42	0.39	16.86	48.94	10.25	12.83	0—50	—	0.5	—	—	P_2O_5
SO_3	2.83	2.64	—	6.52	1.32	6.87	5.58	0—25	2.51	0.4	—	1—12	SO_3
Cl	5.59	0.07	0.27	3.46	0.47	6.20	15.78	0—20	—	—	—	—	Cl
Total	100.93	99.51	100.21	100.57	99.73	101.30	101.57	—	100.38	100.8†)	—	—	Total
Ash-percentage	26.75	0.21	7.20	3.79	2.14	16.48	11.04	0—30	—	—	2—12 and more		Ash-percentage

Table V.

1 Horsetail A.[104]
2 Fir wood B.[105]
3 Oak bark A.
4 Potatoes A.
5 Wheat grains A.
6 Spinach A.
*) stated as Mn_3O_4.

7 Celery. A.
8 Approximate limits for plant ash.
9 Peacock vein, S. Wales C [106]
10 Combined Residue of 4000 samples of Ruhr Coal, Germany. D [107]
11 Limits of Chief Constituents. American Coal Ash. E [108]
12 Limit of Chief Constituents. English Coal Ash. F [109]
†) soluble in water, especially $CaSO_4$, $MgSo_4$ and Na_2SO : 4.8 %

not deviate largely from that of plant ashes. This, however, would be a false conclusion, as during the whole process of sedimentation and carbonization, changes take place, which involve the *introduction* of ordinary sedimentary matter and the *extraction* of easily soluble compounds. The result is, that coal layers with a rather high ash content show a composition of their ash, not very different of many rocks. In the case that the changes which take place, involve rather a loss of substance than an increase of ash content, a concentration-process of difficultly soluble constituents begins and owing to these threefold natural concentration processes — viz. (1) during plant life, (2) during the decomposition of the organic matter and (3) by the action of subterranean circulating solutions — the amount of rare elements in coal ash is sometimes very remarkable. E.g., percentages of 1 % germanium dioxide and 2 % of gallium oxide have been reported.[110]) This clearly shows the necessity of spectroanalytical or other qualitative investigation *of at least one of a larger number of genetically related ash-samples*, before starting the chemical analysis of these same samples, at least in scientific research.

Generally the analysis of coal-ash does not differ essentially from silicate rock analysis.[111]) The range of variation to be expected, is somewhat different from that given for the constituents of rocks and also changes slightly with the different types and localities. See Table V; it will need no further comment.

Coal ash is prepared in the same manner as plant ash, viz. by the incineration of finely powdered coal in an oxidizing atmosphere. Here too, heating to higher temperatures than are required for the carbonization, should be avoided. At temperatures above 850° most ashes melt and become difficultly soluble in acid.

A large part of coal ash is acid soluble. Only the residue need be fused with sodium carbonate. To prevent the separation of silica during solution of the ash, the liquid should be only weakly acid. A suitable amount of ash — generally 1 g — is weighed out and treated at the temperature of the water-bath with dilute hydrochloric acid, 1 : 25, until no more solid matter goes into solution. The liquid is filtered hot into the dish reserved for the dehydration of silica, the filter containing the insoluble matter is transferred moist to a clean platinum crucible, in-

cinerated and fused with six times the weight of sodium carbonate. The melt is dissolved in excess of hydrochloric acid and the carbon dioxide boiled out. The analysis is continued in the usual way.

The determination of the alkalies can best be carried out according to the L. SMITH procedure; the treatment with barium chloride or hydroxide should not be omitted, (p. 78), otherwise considerable amounts of sulphate will contaminate the weighed alkali chlorides in the case of the coal sample containing much pyrite or other sulphur compounds. The procedures for the determination of other constituents will be found in the chapters on the analysis of silicates.

SALT DEPOSITS AND MINERAL WATERS.

In this separate chapter the analysis of the following groups of minerals will be considered, as they are frequently found together in nature:

1. carbonates,
2. sulphates,
3. phosphates,
4. halides,
5. borates,
6. nitrates,
7. iodates, chlorates,
   perchlorates,

mineral waters.

Carbonate minerals. General Considerations.

These minerals form an iso-dimorphous series:

	Trigonal		Orthorhombic.	
	Calcite	$CaCO_3$	Aragonite	
$CaMg(CO_3)_2$	Dolomite		Strontianite	$SrCO_3$
$MgCO_3$	Magnesite		Witherite	$BaCO_3$
$FeCO_3$	Siderite		Cerussite	$PbCO_3$
$MnCO_3$	Rhodochrosite			
$ZnCO_3$	Galmei.			
$CdCO_3$	Cadmiumcarbonate.			

Consequently, isomorphous replacements are the rule and pure salts of one metal are seldom found.

Carbonates of copper, bismuth, uranyl, rare earths and the alkalies are less often found as minerals.

Procedures of general interest for the analysis of carbonate minerals will be found in the paragraphs on the analysis of carbonate *rocks* and on the separation of minerals, p. 130 and 104, and are of special interest if substances other than carbonates (quartz, etc.) accompany the former.

The *general course* of analysis for a very complex mixture of carbonates containing the above elements will be as follows: —

Carbon dioxide is determined preferably according to one of the methods described, (p. 96—98) or, less accurately, by dissolving a weighed amount of the mineral in an excess of 0.1 N HCl, boiling away the CO_2 and titrating back the excess of acid with 0.1 N KOH. Every ml of 0.1 N acid represents 2.2 mg CO_2 or 3.0 mg CO_3''. *Thermal treatments* do not liberate carbon dioxide held by alkalies and barium; in these cases and when the more simple treatment with acid is not used, a fusion with borax will decompose these compounds as well. *Procedure:* fuse 10—12 g borax or 5—6 g of the anhydrous salt in a platinum crucible. When thoroughly freed from any water a correction for volatilization of the borax alone will be necessary. The loss in weight under working conditions during 10' heating is to be ascertained; then, 0.5—1.0 g of the sample is spread out in a thin layer on the surface of the borax. After thorough fusion and long cooling in a dessicator, the loss in weight is determined. In the case of most carbonate-minerals this may be considered to represent $CO_2 + H_2O$.

Other *non-metals* and *water* are determined as has been described in the section on the analysis of carbonate rocks.

The sample reserved for the determination of the *metallic elements* is dissolved in dilute nitric acid. Insoluble part and soluble silica are separated first, p. 40—44. Next bismuth may be removed from the solution as basic nitrate; subsequently, lead and copper are determined electrolytically; cadmium and zinc are precipitated as sulphides, respectively in medium and feebly acid solution; in an ammonia precipitate iron, rarely also aluminium, rare earths and uranium will be caught; manganese is precipitated by ammonium sulphide; calcium, strontium and barium are precipitated as carbonates if magnesium is absent, or as oxalate or sulphates if this does not hold. Alkali-metals, if present at all, must be determined in a separate portion. If sufficient material is available, it will be advisable not to make use of so complex a scheme but to carry out group-separations of most of the metals, before proceeding with the analysis of the alkaline earths. Ordinarily, the work will be much less complicated owing to the rather simple composition of many carbonate minerals.

ANALYSIS OF CALCITE, DOLOMITE AND MAGNESITE.

The methods referred to in former sections, (viz. of carbonate rocks), yield also satisfactory results in the analysis of calcite, and of dolomite containing small amounts of the other above elements. Impure magnesite, containing small amounts of calcium, however, should be analysed according to the sulphate method:

DETERMINATION OF CALCIUM IN MAGNESITE. PROCEDURE OF SULPHATE METHOD.

4 volumes of ethyl alcohol are added gradually to the concentrated sulphuric acid solution of 0.5 g of the air-dry sample, containing a slight excess of free sulphuric acid. After standing overnight, the precipitate is filtered off, washed thoroughly with 70 % alcohol, sucked dry and ignited. The residue is taken up in hot hydrochloric acid. Calcium is re-precipitated as oxalate, (see p. 65, seq.). Magnesium is determined in the filtrate after expulsion of the alcohol.

ALTERNATIVE PROCEDURE. [112)]

The concentrated sulphuric acid solution of 1.0 g of the air-dry sample is evaporated nearly to dryness in an air bath. After cooling, 3 ml water are added and the liquid is evaporated on the water bath until it is of syrupy consistence. 50 ml of a mixture of methyl- and ethyl-alcohol, 9 : 1, are gradually added with constant stirring. After standing 30', the precipitate is filtered off and treated as above. Magnesium is determined in an aliquot portion of the filtrate after the alcohols have been removed by evaporating down the liquid to a small volume.

The following is of interest in the analysis of *silicates*, containing minor percentages of calcium in the presence of much magnesium. When the described procedure is applied on the analysis of these substances, considerable amounts of alkali sulphates will co-precipitate after fusions with alkali carbonates. Therefore HILLEBRAND [113)] advocates the following procedure in the analysis of samples containing much magnesium with traces

of calcium: The precipitation with oxalate is omitted. Calcium then separates as phosphate together with magnesium. The weighed pyrophosphate is dissolved in a small excess (0.5 ml excess) of dilute sulphuric acid (or in nitric acid if resistant to the former procedure) and evaporated to fumes of sulphur trioxide. For every 300 mg of pyrophosphate that were present add 10 ml alcohol of 75 % by volume. After standing overnight, the calcium (strontium, barium) sulphate is filtered off, dissolved in the minimum of hydrochloric acid and is precipitated as oxalate in as small a volume as possible. This procedure is of interest also for the recovery of any calcium that may have escaped the separation as oxalate. If the amount of magnesium is likewise of interest, this element should be re-precipitated in the filtrate after expulsion of the alcohol. Only for very small amounts of calcium, a correction for the presence of this element may be applied on the basis of the normal salt : $Ca_3(PO_4)_2$; factor: 1.83. For larger percentages, this is not allowable, owing to the variable composition of the calcium phosphate. If, either, magnesium is not of interest, or will be determined in the filtrate, the joint precipitate of calcium and magnesium need not be ignited, but is directly dissolved in a small excess of sulphuric acid.

ANALYSIS OF SIDERITE AND RHODOCHROSITE.

Iron is separated as hydroxide by double or triple precipitation with ammonia; manganese is separated as sulphide and determined either as sulphate or pyrophosphate, unless the percentage of this metal is very small in which case it may be determined colorimetrically or gravimetrically as the oxide. Procedures have been described in the chapter on silicate rock analysis, p. 47—64, 92. Iron is largely present in the bivalent state and should therefore be oxidized by nitric acid, bromine water or hydrogen peroxide before the precipitation with ammonia.

The percentage of iron, present in the ferrous form in siderite and other carbonates is determined titrimetrically with standard potassium permanganate solution after dissolving the mineral, preferably in a carbon dioxide atmosphere. Trivalent iron will be found by difference. Procedure: 0.5—1.0 g of the finely divided mineral is dissolved in an Erlemeyer flask in an excess of

dilute sulphuric acid, when necessary with slight warming, and is titrated directly. After the titration, the insoluble part is filtered off. Ferrous iron present in this part of the sample may be determined after decomposition with hydrofluoric acid as described on p. 84—88.

ANALYSIS OF GALMEI AND CADMIUM CARBONATE.

0.5 g of the sample is dissolved in a small volume of *sulphuric* acid and the solution is made 4—5 N with *sulphuric* acid. [114]) The precipitate of cadmium sulphide obtained in the hot solution on passing hydrogen sulphide, is filtered off after cooling. If much zinc is present, a second precipitation is required; therefore, the precipitate is dissolved in hot hydrochloric acid, 1 : 1, and the solution is evaporated to fumes with a small excess of dilute sulphuric acid, 1 : 1. The treatment with hydrochloric acid leaves any copper sulphide, that may be present, undissolved on the filter; copper is weighed as the oxide after ignition. The cadmium sulphate solution in sulphuric acid, obtained after a second precipitation with hydrogen sulphide, is evaporated in a porcelain crucible, followed by heating the residue to 400—500° after which it should be white. A yellow or brown colour is caused by thermal decomposition of the sulphate. The salt tenaciously retains some sulphuric acid. It is therefore dissolved in water, the clear solution is evaporated to dryness, the residue is ignited again and these operations are repeated until constant weight is reached. Factor for CdO : 0,61604.

Zinc is next separated in very weak *sulphuric* acid solution. Ammonia is added until the liquid is neutral, followed by addition of dilute sulphuric acid until the colour imparted to the solution by a few drops of methyl orange just changes. The acidity at the end of the operation should not be more than 0.01 N, otherwise much zinc will be lost. A rapid current of hydrogen sulphide is passed for 45' and the liberated sulphuric acid is neutralized now and then with dilute ammonia if necessary. After 30' standing, the precipitate is filtered off, re-dissolved in sulphuric acid and the procedure is repeated until the precipitate is considered to be free from iron, cobalt and nickel. Ammonium sulphate is present if the solution has been prepared as described and prevents the passage of the precipitate through the filter. The sulphide can be weighed as such

after ignition with sulphur in a stream of pure hydrogen, but the precipitate is preferably converted to oxide by ignition or weighed as sulphate:

The *oxide* is obtained by drying the filter and precipitate in an uncovered platinum or porcelain crucible, followed by carbonization of the paper and oxidation of the carbon formed at as low a temperature as possible in order to avoid reduction to the metal, the latter being comparatively volatile and harmful if a platinum crucible is used. The sulphide is converted into sulphate in the beginning of the ignition, the latter dissociates at temperatures between about 650—950°. The completeness of the reaction — which should be carried out in an adequately oxidizing atmosphere — will be shown by the yellow colour of the zinc oxide at higher temperatures and the heating should not be prolonged too much, nor the temperature allowed to become too high, to avoid loss by volatilization. This is almost certain to take place above 1000°. Conversion to *sulphate* does not offer special advantages. The operation may be carried out, by cautiously dissolving the oxide in dilute sulphuric acid and igniting the dried salt in the same crucible, which has served in the determination as oxide, at a temperature not exceeding 500—550°. Zinc sulphate, like the analogous cadmium and manganese compounds, thus obtained, always contains some sulphuric acid which cannot be removed without decomposition of the sulphate except by repeated treatments with water, followed by drying and ignition of the precipitate. To avoid some of the difficulties which have been mentioned, the sulphide may be dissolved on the filter in hydrochloric acid, evaporated to fumes with a slight excess of sulphuric acid and ignited several times with alternate treatments with water, to constant weight.

The precipitation as phosphate and other methods will not be described here as they are less suitable for the purpose of mineral analysis.

ANALYSIS OF ARAGONITE, STRONTIANITE, WITHERITE AND CERUSSITE.

SEPARATION OF CALCIUM, STRONTIUM AND BARIUM. GENERAL CONSIDERATIONS.

The carbonates of strontium, barium and lead crystallize in the orthorhombic system and are frequently found together with

aragonite. The separation of the alkaline earth metals is consequently a problem which will be rather frequently encountered in the analysis of carbonates and may be treated in this chapter — though being of considerable importance also in the analysis of other minerals — as important methods of decomposition and group separation yield the alkaline earths as carbonates.

Behaviour of the above metals in the regular scheme of analysis.

Lead is best separated as sulphate (or with other elements of the hydrogen sulphide group in acid solution with H_2S) or electrolytically on the anode as lead peroxide. The methods for the determination are described in the next chapter on ore analysis.

Calcium is ordinarily separated as oxalate and is accompanied by most of the strontium only if the latter metal is present in a considerably smaller percentage than calcium. The best separation of the two metals is the one described as the nitrate-nitric acid procedure in the chapter on silicate rock analysis on p. 67. Barium does not separate as oxalate except when present in unusually large amounts. Therefore, if barium is present at all, or strontium in amounts of more than a few mg, the precipitation with oxalate should be followed by a separation of residual strontium and of barium as sulphates. This procedure usually involves the presence of a considerable percentage of alcohol and in the liquid thus obtained the sulphates of the alkalies are also difficultly soluble. In this case HILLEBRAND'S method is preferable viz. separation of the alkaline earths as phosphate together with magnesium and recovery in the weighed pyrophosphate as sulphates. In every case, the sulphates are fused with sodium carbonate to convert them into carbonates. The combined carbonates or oxides are converted into nitrates and a treatment with nitric acid of sp. gr. 1.44—1.46 yields an entirely satisfactory separation of calcium from strontium and barium. With larger amounts of the latter metals, the ether-alcohol method is also applicable, as well as SZEBELLÉDY'S method with isobutyl alcohol, but RAWSON'S method is far less tedious to carry out. Barium is separated from strontium as chromate.

The group-separation as carbonate is less satisfactory, especially when much magnesium is present. The filtrate from a precipitation with ammonia should be evaporated down to about 100 ml and precipitated at 80° with a small excess of ammonium

carbonate solution in slightly ammoniacal medium. The separation is almost always incomplete and a recovery with sulphate is necessary in accurate work.

SEPARATION OF CALCIUM, STRONTIUM AND BARIUM. PROCEDURE.

In the absence of large amounts of alkali salts, the three metals are separated together as sulphates according to the procedure described for the determination of small amounts of calcium in magnesite, (p. 153). Calcium may first be separated with most of the strontium as oxalate. Minor amounts of barium will not co-precipitate and can be separated and determined as sulphate in the filtrate of the oxalate precipitation without the aid of the chromate procedure. With double precipitations, about 10 % of the strontium content will be caught in this precipitate.

Finally, the separation as phosphate together with Mg is applicable. The recovery of the other alkaline earths as sulphates will then be carried out according to HILLEBRAND'S method. (p. 153).

The separated sulphates are collected in a platinum crucible, the filter is incinerated and the sulphates are fused with a fivefold excess of sodium carbonate after thorough mixing with the flux. (The sodium salt is preferable to fusion mixture or to potassium carbonate alone, as potassium causes trouble in the separation of barium sulphate in cases where the sulphur trioxide is also to be determined viz. in the analysis of sulphate minerals. For further particulars, consult the next section on the analysis of sulphates.) The melt is dissolved in water, the residue of this extraction — eventually united with the ignited oxalate precipitate — is dissolved in nitric acid and the excess of the latter is expelled.

SEPARATION OF CALCIUM FROM STRONTIUM AND BARIUM.

RAWSON'S method has been described on p. 67 and effects also the separation of barium together with strontium.

Ether-alcohol method. This procedure gives fairly accurate results only if considerable amounts of barium and strontium are present, otherwise the experimental error becomes of relative enormous influence.[42] The nitrates are dried at 150° in a small Erlemeyer flask of 25 or 50 ml capacity; when completely

dry — ventilation of the air in the flask will be of considerable aid in arriving at this point — and cool, 10 times the weight of absolute alcohol is poured on the finely powdered salts, the flask is corked, shaken gently and allowed to stand for two hours, when an equal amount of absolute ether is added and the flask corked straight away. After standing overnight, the solution is filtered as quickly as possible through a crucible with a sintered glass layer. The residue is washed with the ether-alcohol mixture. Filtrate and washings are evaporated down, calcium is determined as oxalate, p. 64, and examined spectroscopically for the absence of barium and strontium.

SZEBELLÉDY's method [115]) differs from the foregoing procedure in the choice of the extraction liquid. The salts are dried at 130° for one half hour and at 180° for another half hour. After extraction with two 2,5 ml portions of absolute alcohol and one 5 ml portion of perfectly dry isobutyl alcohol, the residue is dissolved in water to liberate inclusions of calcium nitrate, dried as above and again extracted, now with two 5 ml portions of isobutyl alcohol. The filtrates are evaporated down in a weighed platinum crucible and the calcium nitrate is converted into sulphate by an ignition with a five-fold excess of ammonium sulphate. Weigh as calcium sulphate. Factor for CaO : 0.41195.
for Ca : 0.29442.

SEPARATION OF BARIUM FROM STRONTIUM (AND CALCIUM). CHROMATE METHOD. [116])

The residue of the nitric acid- or ether-alcohol-separation is dissolved in a small amount of water and transferred at the same time to a beaker. The solution is neutralized with ammonia, using methyl orange as indicator, excessive amounts of free nitric or hydrochloric acid should be avoided, as ammonium salts other than the acetate are objectionable. 10 ml of a 30 % ammonium acetate solution, neutralized in the same way, are added to yield a buffering action on the acid that will be liberated — acetic acid is harmless — and the liquid is boiled. When still hot, the precipitation is carried out with a slight excess of a 10 % solution of ammonium bichromate free from sulphuric acid. After cooling and standing for one hour the supernatant liquid is decanted from the precipitate through a filter. The pre-

cipitate and filter are washed by decantation with a dilute solution of ammonium acetate (obtained by diluting the 30 % solution with 50 times the weight of neutral distilled water) until the washings are colourless; not more than 100 ml will be required. The small amount of barium chromate on the filter is dissolved in dilute nitric acid and the solution is caught in the original beaker, containing the main mass of the precipitate. The barium chromate will dissolve readily and on the addition of dilute ammonia, is re-precipitated, but not further than to the formation of a small precipitate which does not re-dissolve on stirring the solution. The precipitation is completed by the addition of 10 ml of 30 % ammonium acetate solution, followed by boiling. After one or two hours, the precipitate is collected in a porcelain filter crucible and ignited at a dull red heat. The barium chromate is weighed. Factor for BaO : 0.60532.
for Ba : 0.54221.

If a filter paper is used, the paper and precipitate are dried and the filter is ignited separately. The chromate is added to the ash and the ignition is continued until green spots of chromic oxide, which may have formed, disappear by re-oxidation.

The combined filtrates from the first and second chromate precipitations are boiled to ensure the absence of barium. The clear liquid is evaporated down to a small volume, after being acidified with nitric acid in small excess. Strontium is precipitated at 80° with ammonium carbonate in slightly ammoniacal solution. The precipitate is filtered off, washed with a few ml of hot water and is dissolved in dilute hydrochloric acid, avoiding any undue excess. Ten times the equivalent amount of sulphuric acid is added and an equal volume of alcohol. Strontium sulphate separates and is filtered off after standing overnight, washed with alcohol (75 % by volume) ignited (if a paper filter has been used, precipitate and filter are preferably ignited separately). The precipitate is weighed as $SrSO_4$.

Factor for SrO : 0.56419.
Sr : 0.47709.

BARIUM. DIRECT PRECIPITATION AS SULPHATE. GENERAL CONSIDERATIONS.

The separation and determination of barium as sulphate is preferable in many cases especially when other metals forming

difficultly soluble sulphates viz. Pb, Sr, Ca are absent. Still other elements interfere with this separation by being adsorbed on the precipitate. The matter will be more fully discussed in the next section with the determination of larger percentages of sulphur trioxide as barium sulphate. Cf. also methods for the determination of barium and sulphur in silicate rocks (p. 98 and 100).

MISCELLANEOUS.

Carbonates of lead, copper, bismuth, rare earths, uranyl and alkalies are also found in the mineral kingdom, but generally as products of weathering from other minerals and usually not related with the carbonates, the analysis of which has already been described in the former parts of this section.

Lead. Basic lead carbonate is also an important industrial product (white lead). 0.5—1.0 g of the sample is dissolved in 50 ml dilute hydrochloric acid, 1 : 2, at temperatures not higher than 60°; the solution, diluted with an equal volume of boiling water, is filtered from the residue and the filter well washed with hot water. The insoluble residue is weighed and again weighed after ignition. The separation and determination of lead will be described in the next chapter on ore-analysis.

Copper. Copper carbonate occurs in nature as basic salts of variable composition. The mineral is dissolved as other carbonates but in dilute sulphuric acid and the insoluble residue determined. The solution is electrolyzed (p. 225); copper separates on the cathode, lead, if present as peroxide on the anode. Other metals are precipitated with ammonia, ammonium oxalate, etc. according to known procedures.

Bismuth, uranium and *rare earths* are not often encountered in carbonate analysis and can only be briefly mentioned. Bismuth is conveniently determined by hydrolysis of the aqueous solution of the nitrate, uranium and rare earths are caught in the ammonia precipitate and separated by methods given in other sections.

Alkali carbonates are all easily soluble in water. After separation of other constituents, especially sulphates, the salts are converted into chlorides and are weighed and separated as has been described in the section on the determination of the alkalies in silicate rocks (p. 80, seq.).

SULPHATE MINERALS. GENERAL CONSIDERATIONS.

Though, occasionally, sulphates of most metals are found in nature, either as single salts, or as double salts of two (and even more) metals, and sometimes in combination with salts of other acids, the sulphates of the alkalies and alkaline earth metals are primarily of interest. Most sulphates are water-soluble and will not cause any trouble in preparing a solution for the analysis. Those of the earth alkalies and of lead are difficultly soluble in water and better in hot concentrated acids. Though they are more or less completely attacked by concentrated *solutions* of alkali carbonates (with formation of alkali sulphates and of acid-soluble carbonates), the outstanding method of decomposition is fusion with five- to eight-fold excess of sodium carbonate. The aqueous extract of this melt contains the sulphate ion; the residue consists of acid-soluble carbonates and, after repetition of the former operation, is conveniently analysed according to the methods described in the previous section. Potassium carbonate should not be used to replace the sodium salt either partially or entirely as potassium is co-precipitated to a much greater extent with the barium sulphate.

DETERMINATION OF SULPHUR AS BARIUM SULPHATE. GENERAL CONSIDERATIONS.

In view of the importance of the exact determination of sulphur in either form, the determination as barium sulphate will be considered here more in detail.

The determination of sulphate ion and barium are converse procedures; the former, however, is more liable to error: when *barium* is precipitated from either solution it is immaterial, whether some other barium salt is co-precipitated, provided this salt can be converted into sulphate by a treatment with sulphuric acid, e.g. the chloride, nitrate and chlorate which are frequently co-precipitated.

In the determination of *sulphuric acid* these errors are likewise not inevitable, since by a very gradual addition of barium chloride solution to the hot, diluted sulphuric acid solution, very slight co-precipitation of barium chloride results and this error may *compensate* the error produced by the slight solubility of

the sulphate. When the precipitate is formed by the addition at once of an excess of barium chloride solution, barium chloride will be co-precipitated, but can be determined easily in the weighed precipitate as chlorine ion.

In the determination of *sulphates,* the disagreeable adsorbing properties of barium sulphate cause more trouble in every respect. The ultimate result of these errors cannot be easily foreseen: co-precipitation of barium chloride causes high results, as well as the presence of other acids, especially phosphoric and to a less degree nitric acid. The solubility of barium sulphate of 2.5 mg to the liter is offset by a common ion, but increased by high concentration of mineral acids. On the contrary the effect of mineral acids is advantageous when they are present in small excess (preferably 1 % of hydrochloric acid) as, owing to the greater solubility, barium sulphate is precipitated in a more easily filterable, coarser crystalline form than in neutral solutions and then will not require special filters. Other metals, especially iron, chromium, potassium, sodium and ammonium cause low results, as they are co-precipitated as sulphate, the lighter metals partially replacing barium and in addition, the loss of sulphuric acid (iron sulphate) or even the whole compound (ammonium sulphate) may introduce serious errors.

Consequently it will be best, to determine sulphur only in dilute solutions as free from other compounds as possible. The dilute solution may be made an "extremely dilute solution" by the simultaneous addition, in equivalent amounts, of the sulphate solution and the barium chloride solution to a beaker containing boiling water [117]).

Ignitions in the presence of charring paper will cause reduction of sulphate to sulphide, unless the paper is charred very cautiously at a low temperature without ignition. It is, however, safe to moisten the ignited precipitate with a few drops of dilute sulphuric acid, carefully expelling the excess and to re-determine the weight after again igniting in an oxidizing atmosphere. When no corrections involving further treatment of the ignited precipitate are to be applied, it will be best to use a filter crucible for the filtration and ignite at temperatures not over 900° in this case to avoid decomposition of the sulphate with simultaneous attack of the crucible.

Heavy metals can generally be separated by electrolysis with a mercury cathode [118]). Iron may be removed also by fusing

with sodium carbonate, or by double precipitation at 70° with ammonium hydroxide — double precipitation being required to free the precipitate from sulphate —, or by a single precipitation, using a liberal excess (viz. 50 ml of 0.1 N ammonium hydroxide to prevent the formation of basic sulphate). Iron may be made harmless according to KÜSTER and THIEL [119]) by precipitating it at 70° with a large excess of ammonium hydroxide, then, barium chloride solution is added without preliminary filtration of the iron hydroxide; after complete precipitation of the barium sulphate, the iron hydroxide is dissolved and the precipitate washed clean by a careful treatment with dilute hydrochloric acid. Finally, after reduction of iron to the bivalent form, it will likewise not be co-precipitated.

Ammonium salts should be removed according to the procedure of LAWRENCE SMITH [120]) by evaporation to small volume of the liquid, followed by digestion with nitric acid, 2 ml of the concentrated acid being required for every gram of ammonium chloride. After the addition of the nitric acid, cover the beaker with a watch-glass and when the vigorous gas-evolution has ceased, evaporate to dryness. The nitrates, which may be present are now converted into chlorides by evaporating them down three times with hydrochloric acid. Alkaline earth sulphates are decomposed by fusion with sodium carbonate, followed by extraction of the melt with water. In the same way, sulphur and sulphides can be prepared for the analysis.

In the aqueous solution obtained in either way, sulphate is determined as barium sulphate. The solution should preferably contain 1 % of free hydrochloric acid. Precipitation in hot solution followed by prolonged digestion at higher temperatures is advantageous, a coarser precipitate being formed with only slight contamination by occlusion and adsorption of foreign matter.

PROCEDURE FOR THE DETERMINATION OF SULPHUR AS BARIUM SULPHATE.

Prepare a solution fulfilling the above requirements and preferably not containing more than 0.1 g of sulphate ion per 100 ml. A 10 % barium chloride solution is added dropwise with vigorous stirring *when only slight amounts of alkalies are present.* After the precipitate has settled somewhat, the clear liquid is

tested now and then to ascertain whether the precipitation has been complete. When this is true, the covered beaker is placed on the water-bath and the liquid stirred occasionally. After standing overnight, preferably in a *warm* place throughout; the precipitate is filtered off by decantation of the clear supernatant liquid through the filter followed by transference of the precipitate to the filter and proper but not excessive washing with warm water until barium can be shown to be absent in a few ml of the filtrate.

When considerable quantities of alkali salts are present the addition of the precipitant should be done *at once* with vigorous stirring: the minus error due to co-precipitation of alkali sulphate is nearly compensated by the plus error due to co-precipitation of barium chloride. In this case, in order not to disturb the compensating effect, the solution is filtered off after 30' standing in a warm place and washed properly but not excessively.

The moist filter is placed in a weighed platinum, porcelain or fused silica crucible; the paper is carefully charred without ignition, otherwise mechanical loss will be almost inevitable. After the cover has been put in place, the final ignition is carried out at a temperature of about 900°. Any sulphide, possibly formed during the ignition should be re-converted into sulphate by a treatment with sulphuric acid followed by ignition.

DETERMINATION OF METALLIC ELEMENTS IN SULPHATES. GENERAL CONSIDERATIONS.

The metallic elements are determined according to the methods described in the foregoing section (carbonate minerals) and those which will be given in the chapter on ore-analysis. Elements of the hydrogen sulphide group may be separated in dilute hydrochloric acid solution, provided oxidizing agents are absent and hydrogen sulphide is boiled out directly after the filtration of the sulphides.

DETERMINATION OF WATER IN SULPHATES.

The water of crystallization of sulphates is liberated at various temperatures, near to, or even surpassing the temperatures required for thermal decomposition of the sulphate. Alkali and

alkaline earth sulphates are not decomposed at temperatures high enough to drive off all their crystal-water, viz. at a dull red heat, neither is lead sulphate decomposed at these temperatures. The sulphates of magnesium, manganese, nickel, zinc and copper are all stable at temperatures up to 400° and their water-content can be determined by very careful heating at this temperature. Other sulphates are decomposed at still lower temperatures, but making use of an artifice, their water-content may be determined as loss on ignition, provided no other changes affecting the weight of the sample occur, namely by careful heating of the sample, intimately mixed with pure dry zinc oxide and covered with a layer of zinc oxide in a porcelain crucible. Whilst the water is driven off entirely, the sulphur trioxide will be retained as zinc sulphate. This procedure is rather difficult to carry out.

The following procedure is generally applicable[121]): The sample is weighed out in a porcelain boat and introduced into an apparatus somewhat similar to that used in the analysis of organic substances by combustion. A combustion tube, about 40 cm long, is placed in a small furnace. To retain sulphur trioxide, a layer of a 50/50 mixture of lead oxide and lead peroxide is spread out at the outlet end of the tube. This layer should have a length of 8—10 cm and be heated slightly during the whole determination to prevent it from retaining water. Two fish-tail burners are required, one to heat the layer of mixed oxides, the other to decompose the sample. The outlet end of the tube is drawn out, so as to fit directly into the absorption tube containing calcium chloride. The other end of the tube is provided with a rubber stopper and inlet tube for dried air. The air should be dried with calcium chloride, it being the general rule to use the same reagent in purifying the current of gas, as will be used to catch the gases or vapours liberated by the reaction. The boat with the weighed portion of the sample is placed about in the middle of the combustion tube and the whole heat of the burner is *gradually* applied. Carbon dioxide is *not* retained in the layer of lead oxides, hence the necessity of using neutral calcium chloride when carbonates are likewise present in the sample, or in the case of the water content of carbonate minerals being determined according to this method. Halogens, however will be retained.

PHOSPHATE MINERALS.

The *complete* analysis of natural occurring phosphates is a very complicated task owing to the presence of much phosphorus and the complexity of many phosphates. In most cases, viz. for natural or artificial products, used as phosphorus manure, only the percentage of P_2O_5 will be of interest. In addition to the total percentage of phosphorus pentoxide, the amount, soluble in 2 % citric acid, or in acid ammonium citrate solution, or in water is often recorded, as these percentages are to some degree correlated with the percentage, accessible to plant roots. Consequently, the *methods of analysis* will be divided as follows: 1. Procedures for the determination of phosphorus pentoxide, 2. Procedures for complete analysis.

ATTACK OF PHOSPHATE MINERALS.

Most phosphates can be decomposed by attack with acids and in many cases this will be advisable, as only volatile reagents need be introduced in the solution. Nitric acid decompositions are always preferable when the molybdate procedure for the determination of phosphorus is intended. Aqua regia, however, is of considerable help in attacking difficult soluble substances. Any chlorine as well as silica and fluorine [122]) should be removed by repeated evaporations with nitric acid to avoid the interfering action of these substances in the molybdate procedure. Boric acid may also be used to neutralize the harmful effect of fluorides.

In decomposing with a mixture of sulphuric and nitric acids, most of the calcium is removed already and this will be found preferable if the citric acid method is to be used and also for the molybdate method, though the presence of sulphate ion is in both methods slightly harmful. In some cases, a decomposition with fluxes or fusion of the residue of an acid extraction may be found preferable. A fusion with sodium carbonate or sodium hydroxide yields a preliminary separation of phosphorus from most other accompanying elements that would otherwise interfere with the determinations, especially iron, rare earths, calcium and lithium. As the *fusion* needs ordinarily to be repeated, to save time this separation must, whenever possible, be effected with a sodium hydroxide *solution* after decomposition with acids.

PROCEDURES FOR THE ATTACK.

Natural phosphates are digested with a mixture of five times their weight of concentrated hydrochloric acid and twice their weight of nitric acid (sp. gr. 1.4) on the water-bath and the evaporation with small quantities of nitric acid alone is repeated twice. The residue is dissolved in 50 ml nitric acid, 1 : 5, and the solution is boiled to re-convert the whole amount of phosphorus to orthophosphoric acid. After filtering off the insoluble matter and the silica that may have separated, the solution is ready for the analysis according to the molybdate method. The residue from the decomposition may be treated according to the methods of silicate analysis.

Natural and artificial phosphates may be decomposed with a mixture of 10 times their weight of concentrated sulphuric acid and three times the weight of nitric acid. After heating, the solution is diluted with water until it contains about 10 % by weight of sulphuric acid. Care should be taken not to heat to fumes the sulphuric acid in this decomposition, as serious loss of phosphorus may result. For the same reason, decompositions with pyrosulphate are not permissible, unless when carried out in tightly covered crucibles, for short periods and at temperatures only slightly above the melting point of the salt.

Information of interest for the decomposition with fluxes will be found on p. 49 and 57, (separation with sodium hydroxide solution; fusion with sodium carbonate) and p. 94 (determination of P_2O_5 in silicate rocks). Mere extractions with dilute acids are unsuitable to bring into solution phosphoric acid combined with titanium [123]. This case occurs frequently in soils.

METHODS OF ANALYSIS ON PHOSPHATES.

1*a*. MOLYBDATE METHODS.

The description of this procedure has been given on p. 95. For larger percentages of P_2O_5 the method is not accurate enough, unless when carried out according to some special working procedures, using an experimental determined factor for the calculation of the phosphorus present in the molybdate precipitate. The well-known LORENZ method will serve here; the original description of this method [124] or of any of the well-

known modifications [125]) should be consulted. The completeness of the precipitation should be made certain by using enough of the solutions, 100 ml of the ammonium molybdate reagent being required for every 0.2 g of P_2O_5 present in the solution and the other reagents in proportion; in addition to this the filtrate should be tested by adding a new portion of the reagents.

1b. COMBINED MOLYBDATE AND MAGNESIUM AMMONIUM PHOSPHATE METHOD.

In this method, the precipitation as phosphomolybdate serves only as a preliminary separation in removing interfering substances; consequently the yellow precipitate need not be of definite composition; it may be washed with ammonium nitrate solution and it is not necessary to transfer it to the filter. The whole amount of the precipitate is dissolved in a small volume of 10 % ammonium hydroxide and is filtered into a 400 ml beaker, the filter being adequately washed with a few drops of concentrated ammonia, followed by six small portions of hot water. In the filtrate, phosphorus is precipitated as magnesium ammonium phosphate. Therefore, the required amount of *magnesia mixture* (chloride) is added drop by drop to the slightly ammoniacal solution, the liquid being stirred with a glass rod protected by a rubber ring; this avoids scratching the glass. After complete precipitation, concentrated ammonia water is added until this will occupy about one fifth part of the total volume. The magnesia mixture should be added very gradually, an excess of phosphate is required in the first stages to yield a precipitate of the required composition. A re-precipitation should always be made; therefore, the precipitate is filtered off after standing overnight and is dissolved in a small amount of hydrochloric acid after slight washing. Dilute to the appropriate concentration (0.1 g of P_2O_5 per 100 ml and add a few ml of magnesia mixture. The precipitation is made by gradually adding *dilute* ammonia in slight excess to the acid solution as described in the section on the determination of magnesium in silicates, (p. 69). In the same section the further treatment of the precipitate will be found. The phosphorus is weighed as magnesium pyrophosphate. Factor for P_2O_5 : 0.63776.
for P : 0.27852.

1c. Citric Acid Method.

In most cases, the direct precipitation of magnesium ammonium phosphate is forbidden owing to the presence of iron, aluminium and other elements likewise precipitated in ammoniacal solution. In the absence of excessive amounts of calcium — e.g. after sulphuric acid decompositions or fusions with sodium carbonate or hydroxide — these metals can be kept in solution with citric acid in the form of complexes.

The method, however, is likely to yield low results, owing to the retarded precipitation of magnesium ammonium phosphate in presence of large quantities of citric acid. So, the other procedures are preferable. [44a)]

The solution for the analysis is treated with a sufficient quantity of 10 % citric acid. After having nearly neutralized the liquid with dilute ammonium hydroxide, 1 : 1, the phosphorus is precipitated by adding drop by drop 25 ml of magnesia mixture whilst constantly stirring as in 1b. Finally, one fifth part of the volume of concentrated ammonium hydroxide is added and after standing overnight, the precipitate is filtered off and treated further as in 1b. The concentration of P_2O_5 should not exceed 0.1—0.2 g in 50 ml of the original solution, nor 0.1 g at most per 100 ml of the final solution. With these quantities, about 50—100 ml of citric acid solution (according to the amount of iron and aluminium present), are required.

1d. Phosphorus Pentoxide Soluble in Citric Acid, Acid Ammonium Citrate, or Water.

Details of these methods will not be given, as there is a marked diversity in the recommended procedures. Ordinarily the analyst is bound by a special procedure, in use in the laboratory where the analysis is carried out, or by some other instruction.

2. Methods for the Complete Analysis of Phosphates.

The most important natural phosphate is the calcium salt, ordinarily with appreciable quantities of chlorine, fluorine, or carbonate and accompanied by a large number of other elements. Phosphates of various metals are not rare in nature, viz.

those of lead, copper, zirconium, rare earths, titanium, aluminium, iron, manganese, zinc, uranyll, beryllium and lithium Sometimes they are contaminated with small amounts of arsenic and vanadium and often, mechanically, with other substances.

The chief difficulty in analysing phosphates is caused by the presence of the main element in quantities, prevailing over the other elements in the ammonium hydroxide group, so that either, phosphorus will be incompletely separated, namely when alkaline earth metals are absent, or, the latter will be co-precipitated wholely or partly. The errors affect the percentage of phosphorus, as well as that of aluminium, alkaline earths and magnesium, further troubles may arise in the determination of the alkalies. The methods to overcome these difficulties can be divided as follows: 1. Phosphorus is wholely precipitated in the ammonium hydroxide group, 2. A preliminary separation is carried out.

1. Phosphorus can be entirely precipitated in the ammonium hydroxide group by adding a sufficient quantity of any of the metallic elements belonging to the group. Generally, an amount of pure iron, equivalent to that of the phosphorus, is added. Iron (and titanium) are determined in the ammonia precipitate, phosphorus in a separate portion. Aluminium will be found by difference. The ordinary procedure of silicate analysis may thus be followed. Cf. the section on the analysis of plant ash, (p. 143).

2. In view of the relative rarity of cases where the complete analysis of phosphates is called for whilst the addition of a known amount of pure iron (or aluminium) is undesirable, only the outline of these complicated procedures are given here.

2a. In determining the alkalies after separation of all other elements, phosphorus must be separated according to the molybdate method prior to the precipitation with ammonium hydroxide. It is troublesome to remove more or less completely the excess of reagent and many errors are likely to occur, so that the method can hardly be recommended.

2b. JANNASCH advocates treating the sample at a dark red heat in a current of carbon tetrachloride vapour during two hours followed by two hours at a bright red heat. [126]) The whole amount of phosphorus is removed, accompanied by the iron. These elements are separated according to the citric acid procedure and iron is precipitated either in the form of the sulphide, or as the hydroxide and weighed as oxide. The analysis of the remainder of the decomposition is carried out according to the

methods of silicate analysis after digestion with hydrochloric acid. This method deserves further study. For details the cited papers must be referred to.

2c. Another useful preliminary separation — applicable only when the alkalies are not determined — is obtained by treating the acid solution of the sample with an excess of sodium hydroxide solution (p. 49) or by fusing the sample with sodium hydroxide, or carbonate followed by extraction with water. The residue of these operations — repeat if necessary — contains part of the silica; titanium, zirconium, rare earths, iron, alkaline earths, magnesium, lithium etc. and may be treated according to the methods of silicate analysis. The solution contains phosphorus, sulphate, chloride, arsenic, antimony, tin, manganese, tungsten, uranium and, for the chief part, silica.

By repeated evaporations with nitric acid, silica and tungsten are separated; a treatment with hydrogen sulphide removes lead, copper, arsenic, antimony etc. (lead alone, may be also separated as sulphate). Phosphorus is precipitated as molybdate; the reagents used, should be as free from aluminium as possible. Finally, aluminium is determined as oxide after double precipitation with ammonium hydroxide. A preliminary extraction of the molybdenum with ether in hydrochloric acid solution will not be necessary.

An estimate must be made of a number of constituents in *separate* portions of the sample, e.g. for manganese, water, fluorine, chlorine, boron and sulphate.

Water is generally determined by the method of loss on ignition, a platinum crucible with the substance is heated over a micro burner until constant weight is obtained. It may also be weighed directly, the sample being heated in a combustion tube with a layer of lead oxides (p. 166) connected with an absorption-train.

Fluorine should be determined as calcium fluoride after distillation with acid, preferably in a small platinum apparatus, the distillate being caught in sodium hydroxide, or according to the methods referred to in the references cited. [127])

Chlorine is determined by dissolving the sample in nitric acid, containing enough silver nitrate to form silver chloride. The latter compound is separated from the insoluble matter by extraction with dilute ammonia, 1 : 1, followed by re-precipitation with nitric acid.

Boron is determined in the usual manner, if present at all.

Sulphate should be estimated by precipitation with barium chloride in hydrochloric acid solution, but preferably after a sodium carbonate fusion in the aqueous extract of the fused cake.

HALOGEN MINERALS.

The *fluorides* are treated separately from the other halogen minerals as the methods for the analysis of both groups are entirely different.

FLUORIDES. GENERAL CONSIDERATIONS.

The most important natural fluorides are the calcium salt, fluorspar, the sodium aluminium double salt, cryolite, and a number of rare earth fluorides. The metals aluminium, iron and the groups of the rare earths, alkaline earths and alkalies have been found to be present in most natural fluorine compounds, though often in subordinate amounts. Ordinarily all of these are worth consideration in mineral analysis.

Fluorine is determined in these substances by the same method as described in the section on mineral analysis, (p. 120). Approximately 0.2 g of the mineral is weighed out and mixed thoroughly with the same weight of pure silicic acid free from fluorine and 10 times the weight of the fusion mixture of equimolecular amounts of sodium and potassium carbonates. Further procedure of the analysis will be found in the section referred to.

The metallic elements are determined in another portion of the sample after decomposition with sulphuric acid. The mixture is heated until copious fumes of sulphur trioxide are liberated, then, after cooling, the mass is diluted with water and a few ml. of sulphuric acid, 1 : 1; the operation is repeated until fluorine is considered to be completely removed (etching-proof). It is evident that a platinum basin or crucible should be used throughout these operations. Fluorine must be completely removed from the solution, to prevent this element interfering with the subsequent separations, especially of aluminium and calcium. After the decomposition, the procedure of silicate analysis may be followed. The alkalies are determined after preli-

minary separation of all the other metals; the alkali sulphates should be converted into chlorides, unless when only one of them is present (spectroscopic examination) whence this metal (ordinarily sodium) may be weighed as sulphate.

CHLORIDES, BROMIDES AND IODIDES. GENERAL CONSIDERATIONS.

These metalloids occur in a large variety of compounds with numerous metals. Most of these substances, however, are mere curiosities; important among them are only the halogenides of the alkalies, ammonium and silver and perhaps also some oxy-chlorides and fluorides) of other elements, especially lead and copper. Quantitatively, the chlorides predominate, but according to the higher economic value of the other salts, methods for their exact determination in mixtures are very important. In some oxy-salts chlorine and fluorine occur combined.

Heavy metals should preferably be separated before the determination of the halogens is started. In the absence of interfering substances and especially when only one of the halogens is present, titrimetric procedures for the determination are nearly as accurate as gravimetric procedures and are preferred as they are more rapidly carried out. This subject is extensively discussed in manuals of titrimetric analysis.

Except for some special titrimetric methods [128]), the separation of the halogens is a necessary condition for the exact determination. Difference-methods are satisfactory, *when the constituent present in small amounts is determined directly;* indirect methods must never be used, though these have often been recommended for the determination of the halogens. Consequently, the separation and the gravimetric determination of these elements are described herein.

SEPARATION OF THE HALOGENS. GENERAL CONSIDERATIONS.

With fluorides, only chlorides are known to occur together. These elements will not interfere with each other in their methods of determination. The same cannot be said from chlorine, bromine and iodine; indeed, the exact determination of these

elements in mixtures is a rather difficult task. Some peculiar differential titrimetric methods are available. The various methods for the separation of the halogens are all based upon the possibility of the expulsion of elementary iodine and bromine, respectively in weak and more strongly oxidizing media and on the titer constancy of very dilute solutions of hydrochloric and hydrobromic acids which may be boiled without loss of

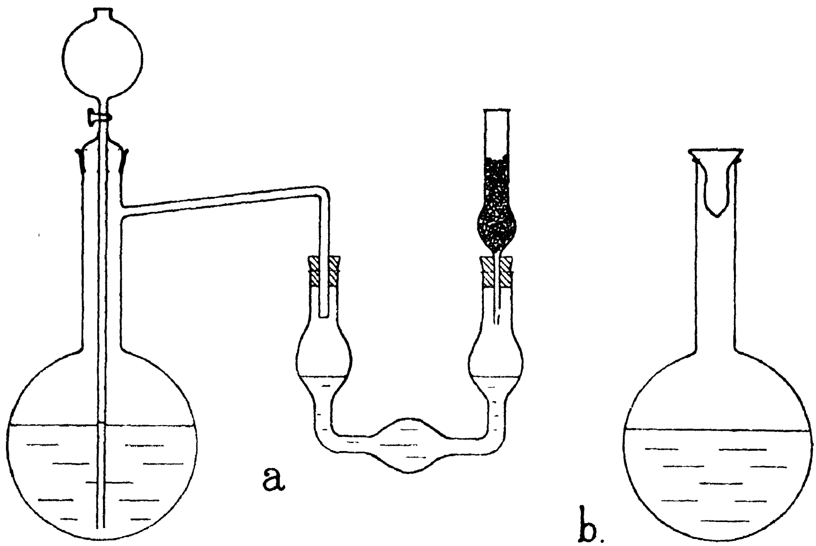

Fig. 11. Apparatus for the determination of the halogens.

combined halogen. The liberated iodine or bromine is caught in a suitable absorption apparatus and may be estimated by titrimetric or gravimetric procedures, or the determination is carried out *by the difference* in determining the halogen remaining in solution after oxidation, (GOOCH'S method).

For the difference methods, only a 1000 ml Erlemeyer flask is required. When the liberated halogens are to be *absorbed*, a distillation flask with ground glass stopper and inlet tube is required. According to the substances used to oxidize the halogenides, a flask of 400 ml or one of 1000—1500 ml capacity will be necessary. The side tube of the flask is connected with a Péligot tube, or some other form of absorption apparatus for use with liquids, the free end of this instrument being protected against loss of the volatile halogens by a vertically projecting

tube with glass rings or pearls, moistened with the absorption liquid. Fig. 11 a and b.

For the expulsion of iodine, either of the following oxidizing reagents is used: 1. nitrous acid (as nitrite), 2. arsenic acid or 3. iron III-sulphate. The iodine may be caught either in a 10 % solution of KI and is titrated with standard solution of sodium thiosulphate, or in an alkaline solution of hydrogen peroxide; then the iodine may be determined gravimetrically as silver iodide.

For the quantitative oxidation of bromides in presence of chlorides the following reagents are suitable: 1. potassium dichromate, 2. potassium permanganate, 3. potassium biiodate, 4. telluric acid.

Bromine is determined after absorption in suitable reagents or the *excess* of biiodate used in the third method may be determined.

Chlorine is ordinarily determined gravimetrically in the remaining solution, or by difference.

PROCEDURES FOR THE SEPARATION OF THE HALOGENS.

Soluble halogenides are prepared for the analysis by dissolving a weighed quantity of the salt in water. Insoluble minerals must be decomposed, the usual method being fusing the substance with five times the weight of sodium carbonate in a porcelain crucible, (a platinum crucible would be destroyed by the liberated metals, viz. silver etc.). The fused cake is extracted with water, the chlorine going into solution. When interfering substances are still present in the liquid, their separation will be necessary before the gravimetric determination as silver halogenide. To prevent adsorption of halogens by the precipitates, the latter should be digested during some time with the solution of the precipitant, or double precipitations will be required, the former method serving for precipitations with hydrogen sulphide (Sn, Sb, Hg) the latter in precipitations with ammonium hydroxide (Al, Fe). Any excess of hydrogen sulphide is removed by boiling the solution and meanwhile introducing a current of water vapour in the liquid, followed by destruction of the last traces with hydrogen peroxide and boiling away the excess of this reagent.

EXPULSION OF IODINE. NITROUS ACID PROCEDURE.

Prepare the apparatus of fig. 11a or take a simple 1000 ml flask when GOOCH's method is preferred. [129]) Dissolve approx. 0.5 g of the sample in 600 ml water, add 4 ml of sulphuric acid, 1 : 1, and introduce 2 g of pure sodium nitrite in the flask. Immediately replace the stopper with inlet tube (or in GOOCH's method the convenient toadstool [130])) and proceed with the distillation. When the liquid begins to boil, complete expulsion of the iodine will be promoted by introducing a current of water vapour *into the liquid* through the long tube; this will also avoid lessening the volume too much.

After the apparent complete separation of iodine, the heating is continued some five minutes, then the connections are freed. Care should be taken in this manipulation to avoid backflow of the liquid in the absorption tubes; the current of water vapour should be continued, until the absorption apparatus is liberated.

When the ferric sulphate procedure is preferred, instead of sodium nitrite, 2 g of iron III-sulphate or the equivalent of ferric alum together with 3 ml of nitric acid are used; in this case it will be advisable, to test the completeness of expulsion by adding another ml of nitric acid and again heating the liquid. Therefore, and because of the introduction of iron in large quantities, this method is not recommended, when pure nitrite is available.

With the arsenic acid method, a much smaller apparatus of about 400 ml capacity will serve. 0.5 g of the sample and 2 g of pure, primary potassium arsenate, KH_2AsO_4, are dissolved in 100 ml of water and 20 ml sulphuric acid, 1 : 1, are introduced. The further treatment as described above. The volume should not be allowed to decrease below 70—60 ml. This method is preferable when the further separation of bromine from chlorine is required, owing to the smaller volume of the solution.

CALCULATION OF IODINE CONTENT OF THE SAMPLE. GOOCH'S METHOD.

When GOOCH's method has been employed, the iodine content of the sample cannot be directly determined. An estimate of the total amount of chlorine and bromine, can be found in the solution after the expulsion of iodine, either by gravimetric, or titrimetric procedures. In another portion of the sample, the

total of halogenides is determined by the same method (namely gravimetrically or titrimetrically) and the difference between these results indicates the weight of iodine present in the sample.

ABSORPTION APPARATUS. FURTHER TREATMENT.

The absorption apparatus contains 10 % potassium iodide solution if the liberated iodine is to be *titrated* with 0.1 or 0.05 N sodium thiosulphate solution, or 100 ml of a 50/50 mixture of 5 % sodium hydroxide solution and 3 % hydrogen peroxide if the *gravimetric* determination as silver iodide is intended. In both cases, the tubes should be effectively cooled, preferably with ice-water, to prevent loss of halogens in the first, excessive formation of iodate in the second case. For particulars concerning the titrimetric procedure, reference should be made to the treatises. [130]

The gravimetric determination is carried out as follows [131]: The alkaline solution is boiled to remove the excess of hydrogen peroxide; on acidifying the cooled solution with pure, dilute sulphuric acid, 1 : 1, a yellow colour will appear, as the formation of some iodate cannot be entirely avoided. This iodine is reduced by the addition of a few drops of sulphurous acid solution (SO_2). A slight excess of 5 % silver nitrate solution is added whilst constantly stirring and the liquid is heated, to obtain the silver iodide in an easily filterable form. The precipitate is filtered off into a filter crucible and weighed after drying at 130—150° in a stove. See also p. 123. Factor for I: 0,54050.

EXPULSION OF BROMINE. POTASSIUM DICHROMATE PROCEDURE.

Only the potassium dichromate procedure and the potassium biiodate method will be described in detail. For the potassium permanganate and telluric acid methods, reference to the original papers will be sufficient. [132]

For the determination of bromine according to the dichromate method, preferably the residue from the distillation with arsenic acid should be used. The same apparatus as for the determination of iodine will serve here also. The solution in the distilla-

tion flask is diluted with 200 ml of water and 50 ml of 20 % potassium dichromate solution is introduced into the flask. The bromine is distilled off and finally a current of water vapour is introduced to make the separation complete. The further treatment will be as described in the foregoing sections for iodine, viz. titration with standard thiosulphate solution or gravimetric determination as silver bromide. Factor for Br: 0.42549.

EXPULSION OF BROMINE (AND IODINE). BIIODATE METHOD.

Bromides and, *a fortiori* also iodides can be quantitatively oxydized in acid solution by iodic acid. The excess of iodate may be titrimetrically determined or may safely be removed. Consequently, small quantities of, either chlorine, or bromine may be accurately determined with the aid of this reagent, provided an exact known quantity of it be used in the form of a solution of known strength. The titer of the solution of potassium biiodate used in these determinations is estimated by adding an excess of KI as concentrated solution to 30—40 ml of the iodate solution, acidifying with a few ml of sulphuric acid, 1 : 1, followed by titration of the liberated iodine with standard thiosulphate solution.

To determine small amounts of *chlorine*, ANDREW's method is applied.[133] Approx. 0.2 g of the sample is dissolved in 200 ml water, contained in a Kjeldahl form flask of 500 ml capacity and the calculated amounts of the iodate solution and 2 N nitric acid are added. The inclined flask is heated to gentle boiling with the small flame of a Bunsen burner, the flask being inserted in the hole of a piece of asbestos, so that only the part filled with liquid will be directly heated by the flame. After 5' boiling, allow the flask to stand overnight, then the volume is reduced to no less than 90 ml in about half — to three quarters of an hour. After the addition of 100 ml water to the somewhat cooled flask, proceed with heating until 50 ml are evaporated, then carefully introduce the steam — with the aid of a pure rubber stopper and bent tube — into a test tube with a few ml of 2 % potassium iodide solution, acidified with a trace of hydrochloric acid. The *complete expulsion of bromine* is secured (no yellow colour should be visible within 1'). The excess of iodate is decomposed by the addition of 1—1.5 ml of phosphorous acid

or any other suitable reagent which will not interfere with the subsequent determination of chlorine. The boiling should not be interrupted when the phosphorous acid is introduced and should be continued 5' after the apparent expulsion of iodine. The volume should not be lessened to more than 90 ml during this operation. The chlorine is determined gravimetrically or titrimetrically from the obtained solution.

To determine small amounts of *bromine*, BUGARSZKY'S procedure should be applied. [134]) The portion is dissolved in the 500 ml flask in 200 ml of water and a known volume of biiodate solution is introduced — a slight excess over the required quantity being essential — followed by 10 ml cold sulphuric acid, 1 : 5; then the flask is heated until the liberated bromine (and iodine) are completely removed (test, as above described). Concentrate to 60—70 ml over the flame and allow to cool. An excess of 10 % potassium iodide solution is added and the excess of iodate is determined by titration with standard solution of sodium thiosulphate, add some starch solution towards the end of the titration. Expressed in ml of 0.05 N thiosulphate solution the factor for the quantity of bromine will be 0.00333 and will have the double value for 0.1 N solutions.

In the same liquid chlorine may be estimated titrimetrically according to VOLHARD'S method after the expulsion of the iodine by heating the solution with a sufficient quantity of sodium nitrite, as described above in GOOCH'S procedure for the determination of iodine.

When *small* amounts of bromine or iodine are to be determined in presence of large quantities of chlorine and bromine respectively, it will be best to proceed with the determination as prescribed by BOEKE for the analysis of carnallite [135]) — $KCl.MgCl_2.6aq$, with fractions of a percent of bromine —. The first distillation is carried out with stated quantities of reagents, with larger portions of the sample (10—50 g). The absorption apparatus is filled with water containing 1 g of sodium or potassium hydroxide. After 20' boiling, heat again 20' in a current of carbon dioxide or water vapour. The absorption apparatus is expressly not efficiently cooled, so as to lead to the formation of bromate or iodate.

After the expulsion is considered to be complete, the contents of the receivers are washed in a 300 ml Erlemeyer flask and are heated with 2 g of pure zinc powder, a short stemmed funnel

being placed in the neck of the flask to prevent loss by spluttering. The bromate is reduced to hydrobromic acid. With this liquid, the operation is repeated in the usual manner. The first distillate will contain some chlorine which is retained for the second time.

GRAVIMETRIC DETERMINATION OF CHLORINE (BROMINE, IODINE).

In ordinary cases, namely in the absence of large amounts of impurities, a 0.5 g portion of the sample is dissolved in about 200 ml water and 10 ml of chlorine free dilute nitric acid (2N) is added. The precipitation is carried out, adding drop by drop of a 5 % silver nitrate solution to the warm liquid, under constant stirring with a thin glass rod. This will cause the precipitate to unite in larger flocculating masses and this property enables the chemist to decide if the precipitation is complete, any considerable excess of the precipitant being harmful, owing to the tenacious absorption of silver nitrate by the precipitates. After standing overnight, the clear liquid is decanted through a weighed filter crucible and the precipitate is washed in the beaker with a few small portions of water acidified with nitric acid, until the precipitate is free from silver nitrate (test). Only then, the precipitate is transferred to the crucible with the aid of a jet of water from the wash-bottle and finally washed free from any nitric acid with a few drops of water in the crucible. Crucible and precipitate are dried in a stove at 130—150° or over the free flame until the precipitate only just begins to sinter.

After cooling in a dessicator, the weight of the crucible with precipitate is determined. Throughout the whole procedure the precipitate should be protected against direct daylight and strong artificial light sources. Factor for Cl: 0.24730.

The solution, remaining in the distillation flask after the expulsion of bromine, contains a considerable amount of impurities, especially chromate. To avoid precipitation of silver chromate, the liquid is strongly acidified with chlorine free nitric acid and after diluting in a 1 l beaker to about 500 ml, the precipitation and determination are carried out as described above. When a dark red precipitate of silver chromate is formed notwithstanding this, more nitric acid is required.

Bromine and iodine or mixtures of the halogens are determined in exactly the same manner. Again, *silver* may be precipitated by any of these three halogens preferably in the form of their alkali salts. Ag Cl ; factor for Ag : 0,75273.

Ag Br ; : 0,57451.

Ag I ; : 0,45947.

BORATE MINERALS. GENERAL CONSIDERATIONS.

Borates may be treated according to the procedure described in the section on mineral analysis; boric acid is determined in the distillate with gravimetric or titrimetric methods. In various cases of easily soluble borates which do not contain substances, interfering with the titrimetric determination, however, the preliminary separation may be omitted. Particulars will be found in the section referred to and in manuals on titrimetric analysis. [136])

NITRATE MINERALS AND AMMONIUM SALTS.

Nitric acid may be determined according to one of the following methods: 1. gravimetrically as nitron nitrate, 2. titrimetrically as ammonium hydroxide, 3. titrimetrically after oxydation of an excess of ferrous salt with the nitrate, 4. with gasometric procedures, e.g.as NO [137]).

The second method includes the procedure for the determination of $NH_4^{\cdot}$

1. NITRON METHOD. PROCEDURE. [138])

A portion of the sample, containing approx. 0.1 g of NO_3' is dissolved in 100 ml of water and 1 ml of dilute sulphuric acid, 1 : 4. This liquid is heated almost to the boiling point; then, 10—12 ml of nitron acetate solution is added at one pouring. The beaker is placed in ice cold water and after standing two hours, the clear, faintly yellow liquid is decanted through a glass sintered filter crucible; the precipitate is brought on the filter, completely sucked dry and washed with 10 ml of ice

water in small quantities at one time. The amount of washing liquid should be as small as is consistent with thorough washing as nitron nitrate is not very insoluble, (approx. 10 mg per 100 ml of acidified water). This loss is counterbalanced more or less by the adsorption of some nitron acetate. The crucible with the precipitate is dried at 110° in a stove and weighed after cooling in a dessicator. Factor for NO_3' : 0.16530.

Various acids interfere with this determination as they likewise yield insoluble compounds with nitron. Among these, chloric, perchloric and chromic acids are to be especially mentioned, as their salts occur together with nitrates in the raw Chile salpeter. In nitrate deposits, the percentage is generally so low that it has no serious effect (less than 1 % of perchloric acid in 0.2 g portions and the above volume of liquid). TREADWELL [139]) states that the following quantities of acids will remain in solution at ordinary temperatures in 100 ml of slightly acidified water, in the presence of nitron acetate: HBr : 125 mg; HI : 5 mg; HNO_2 : 22 mg; $H_2Cr_2O_7$: 11 mg; $HClO_3$: 22 mg; $HClO_4$: 2 mg; (HCNS : 7 mg). Nitron iodate is easily soluble, consequently, iodates do not interfere here. In case of doubt, it will be advisable to ascertain the percentages of these substances, before proceeding with the actual determination of nitric acid according to this method. Hydrobromic acid can be decomposed by adding chlorine water to the solution and boiling away the liberated bromine; hydroiodic acid by adding a sufficient quantity of potassium iodate and boiling out the iodine; nitrous and chromic acids are reduced by hydrazine sulphate: prepare a 5 % solution of the sample in water and add drop by drop on finely pulverized hydrazine sulphate. In the case of chlorates and perchlorates in quantities higher than the amounts stated, the second method should be used.

2. TITRIMETRIC DETERMINATION OF NITRIC ACID, AS AMMONIUM HYDROXIDE. DETERMINATION OF AMMONIAC.

A distillation apparatus is required as represented in fig. 12 a or b, the latter form being preferable, as the operation wil consume much less time. The glass bulbs between distillation flask and condenser serve to avoid mechanical contamination of the absorption liquid by droplets of the alkaline solution, transported by the water vapour. The outlet of the condenser tube projects below the level of the liquid in the absorption flask, so that all the ammoniac will be caught. To promote a more rapid expulsion of ammoniac, a current of water vapour from the generator "G" may be introduced into the liquid. Also it will be necessary, to place a small flame under the distillation flask to avoid the condensation of too much water. To prevent backflow of the liquid, at the end of the operation, lower the absorption flask. A few particles of pumice or unglazed porcelain in the heated flask will avoid bumping of the liquids.

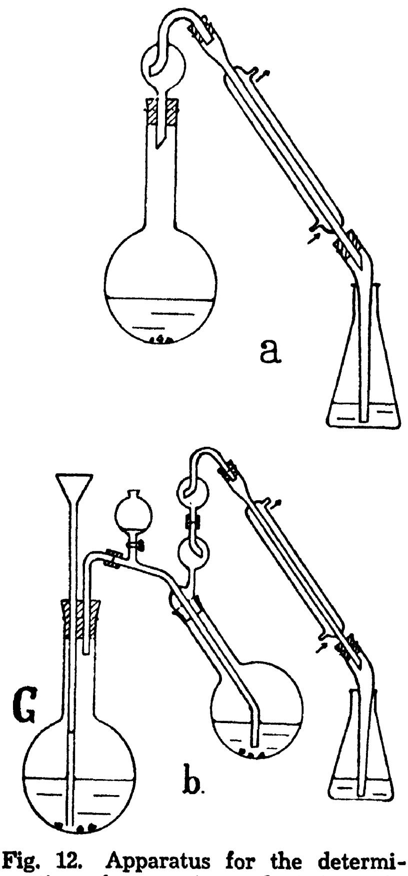

Fig. 12. Apparatus for the determination of ammoniac and nitric acid.

The *quantitative* absorption of the liberated ammoniac may be secured by introducing the vapours through a piece of tubing closed at the end by a sintered glass disc with wide pores. These can now be obtained in different forms. Generally this precaution need only be observed when the distillation is made with a rapid current of water vapour or air.

a. DETERMINATION OF AMMONIAC.

10 g of a representative portion of the sample are dissolved in a measuring flask and the solution is made up to 1 l, when a high grade product is to be analysed and to 500 or even 250 ml for a lower percentage. With the aid of a pipette, 50 ml are taken for the analysis and transported to the distillation flask. 100 ml water, 5 ml alcohol and 5 g magnesium oxide are added, or alternatively, 5 ml of a concentrated sodium hydroxide solution. 1 : 3. The distillate is caught in 100 ml of 0.1 N *mineral* acid (not oxalic acid). Approximately two-thirds of the liquid is to be distilled off and the excess of acid is determined by titration with 0.1 N standard solution of alkali hydroxide, using methylorange as indicator.

To avoid the necessity of a prolonged distillation and the possibility of loss and error, the operation may be shortened by distilling off the ammoniac in a current of steam after PREGL.[140]) Then the apparatus of fig. 12b is used. This will enable the chemist to work with smaller portions, as in fact, the original intention of PREGL was to describe a micro method. A current of ammoniac-free air, nitrogen or hydrogen will also serve; at the same time this will avoid bumping in an effective way.

A determination with the reagents alone must always be carried out under exactly the same conditions, as the amount of absorption liquid consumed in this blank is almost never negligible, notwithstanding the precautions taken.

Ammonia may also be determined by making use of the process mentioned in the description of analytical methods for the ammonia precipitate, p. 60. The excess of bromine is held in the solution by the addition of potassium bromide and titrated back iodometrically. $2\ NH_4^{\cdot} + 3\ Br_2 = N_2 + 8\ H^{\cdot} + 6\ Br'$. [141])

b. DETERMINATION OF NITRIC ACID. GENERAL CONSIDERATIONS.

In the determination of nitric acid as ammoniac, reduction is obtained by heating the solution with reagents such as DEVARDA'S alloy (50 Cu — 45 Al — 5 Zn), ARND'S alloy (60 Cu — 40 Mg) or pure metallic iron. [142]) The original procedure of DEVARDA (working with high concentrations of alkali) only yields correct values by counterbalance of plus and minus errors. There is a

recent modification, due to DONALD, wherein the reduction is carried out with much smaller concentrations of alkali [143]); the methods of ARND [144]) and ULSCH [145]) are also suitable, especially the latter when in the remaining solution (after the determination of ammonia and nitrate) organic nitrogen is to be determined according to KJELDAHL, (for example in analyses of soils and other mixtures, containing organic and inorganic combined nitrogen, as decaying organic matter, etc.); only small quantities of foreign matter need be introduced into the solution, but DONALD's method is equally satisfactory in this regard.

In all these procedures, except the original one of DEVARDA[143]), the contamination of the absorption liquid by spluttering is almost negligible, a blank determination, however, should never be omitted as the reagents may contain considerable quantities of nitrogen in either state.

DESCRIPTION OF DONALD'S PROCEDURE.

According to DONALD, the optimum conditions for the reduction and for the expulsion of ammonia are as follows [143]): 1 g of nitrate, 3 g of DEVARDA's alloy and 2 g of pure solid sodium hydroxide are placed in the distillation flask and 250 ml water are added. The further description need not be given as it will be exactly similar to the one described in the procedure for the estimation of ammoniac. The author's preference is not to take more than 0.5 g nitrate with the above quantities of reagents, otherwise the quantity, or the strength of the absorption liquid should be increased with some 50 %.

DESCRIPTION OF ARND'S PROCEDURE. [144])

Concerning the preparation of the solution, the principles laid down in the section on the determination of ammonia are also applicable in this case. The solution for the analysis is diluted to 300 ml. The hydrolitic dissociation of magnesium chloride solution provides the pH required for the reduction and the liberation of NH_3. 10 ml of a 20 % solution of magnesium chloride and 5 g of finely pulverized ARND's alloy are added. Proceed quickly with the distillation until 200 ml are distilled off,

or make use of a current of steam or air, to increase the speed of the process.

Further details, viz. absorption of the distillate, back-titration of the excess of acid, etc. are the same as described in the previous section.

DESCRIPTION OF ULSCH' PROCEDURE. [145]

The solution for the analysis is prepared as in former methods. A quantity of this liquid containing approx. 0.15 g of nitrate is transported to the distillation flask and 1.5—2.5 g iron powder is added, followed by 5 ml dilute sulphuric acid, 1 : 3. The liquid is gently heated to boiling point and when the evolution of hydrogen has finished and water vapour has been liberated for a few minutes, cool under the tap, add 8—10 ml sodium hydroxide solution, 1 : 3 and proceed with the distillation. The distillate is caught in 50 ml of 0.05 N acid. Owing to the large amount of iron hydroxides present, the time required for distillation is increased; but is shorter in comparison with the above processes, as the volume of liquid is much smaller here. To liberate all the ammoniac, 20—25' is generally found to be sufficient.

DETERMINATION OF AMMONIAC AND OF NITRIC ACID IN ONE SAMPLE.

Nitrogen occurring as ammoniac is first distilled off in alkaline medium, then any of the described procedures for the determination of nitric acid may be used. Organic matter not attacked by these operations can be destroyed, using KJELDAHL'S well-known method and the nitrogen content of it estimated after distillation [146].

Minute percentages of nitrate and ammonia, such as occur in natural water may be estimated according to special colorimetric procedures [147].

IODATE MINERALS. GENERAL CONSIDERATIONS.

Iodate minerals never occur alone, but always in combination, especially with nitrates (owing to the high oxydation potential

in nitrate deposits.) The outstanding procedure of determination for iodates (and bromates) is the titrimetric method based on the equation:

$$KIO_3 + 5\,KI + 6\,HCl = 3I_2 + 6\,KCl + 3\,H_2O$$

Either iodate, iodide or free acid may be estimated with this convenient method.[148] The liberated iodine is titrated with standard sodium thiosulphate solution. For details, the treatises on titrimetric analysis should be consulted. Iodates may also be determined gravimetrically with silver nitrate after reduction with sulphur dioxide; this procedure is not recommended.

Generally, bromates have not been found in the analysis of raw nitrates, though they may be expected in small amounts

described in the determination of alkalies according to LAWRENCE SMITH, p. 77—79. Instead of a platinum crucible (which will be seriously attacked), a porcelain crucible may be used, but the addition of 1 ml of platinum chloride solution is necessary to completely decompose the perchlorate. In mixtures, chloride is determined directly; chloride and chlorate together after reduction with ferrous sulphate; the three compounds, chloride, chlorate and perchlorate together, after a treatment with ammonium chloride. Perchlorates are *not* reduced by ferrous sulphate.

MINERAL AND OTHER NATURAL WATERS. GENERAL CONSIDERATIONS.

Between so-called mineral and other natural waters, no sharp limit exists and the methods for their analysis may be treated in one paragraph. This is placed at the end of the chapter on the examination of salt deposits, as the residue obtained after evaporation of natural waters shows in many regards relation to these substances.

The variability of natural waters and the diversity of chemical elements detected in them, is clearly shown in chapters III—VII of CLARKE's Data of Geochemistry [21]. As, for most purposes, in addition to the chemical constituents, the knowledge of physicochemical and bacteriological data is generally required for a complete investigation of a given water sample, the analysis of potable and other waters has become the domain of specialised chemists and official laboratories. A brief outline of these methods will only be given, for details, the chemist will generally be bound by special regulations; these will partly be found in specialized manuals. [149]

COMPLETENESS AND STATEMENT OF WATER ANALYSES.

As stated above, numerous chemical elements occur in waters; the most important among them being: Cl', SO_4'', CO_3''. HCO_3', CO_2; $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Na^{\cdot}$, $K^{\cdot}$; SiO_2, Al_2O_3, Fe_2O_3, Mn_3O_4. With regard to the latter four, no definite conclusions can generally be made as to the state of their chemical relationship, owing to the small quantities in which they occur in most natural waters. The elements Ca, Mg, Na, K and the radicles chlorine and sulphate

are exclusively present as ions in the liquid, whilst carbon divides, as part of it may be present in ordinary solution as free carbon dioxide. Other compounds which can generally be detected are for example: NO_2', NO_3', NH_3 and $NH_4^{\cdot}$, PO_4''', Br' and boron (as borates). In certain mineral waters, or in larger portions of *most* natural waters, or by spectrographic methods, the following elements also have been detected: I, F, As, Li, Rb, Cs, Ba, Sr, Ni, Co, Pb, Ag, Au, Ra; (refer to BUNSEN and KIRCHHOFF [150]), CLARKE and FITCH [21]), [8]). For the *division* of natural waters refer to CLARKE, p. 183,

> "they are classed according to their negative radicles as chloride, sulphate, carbonate or acid waters, with various mixed types and occasional examples in which unusual combinations, such as nitrates, borates, sulphides, or silicates appear."

It will be advisible to record the analysis of a water in terms of ions as much as possible, either as percentage of total solid matter, together with this sum in parts per million, (= salinity), or simply every ion in parts per million. For convenience and for control purposes it is better to calculate from either of these series of values the molecular proportions of the radicles, by dividing the percentages by their appropriate equivalent weights. The algebraic sum of the electropositive and electronegative radicles in these terms should be zero or as near to zero as can be expected in view of the inevitable errors of the analysis, (ion-balance). In most cases SiO_2, Al_2O_3, Fe_2O_3 (not FeO) and higher manganese oxides are reported as such. In case of a discrepancy between electropositive and electronegative radicles, there may be part of the silica or other mentioned oxides in true solution and the possibility may be born in mind of hydrogen ions or hydroxyl ions being present. This, however, should be considered from fall to fall.

NECESSITY OF PERFORMING DETERMINATIONS ON THE SPOT.

Part of the determinations, namely of components that may change or escape during transportation, must be done at the place where the sample is taken. Therefore a more or less complete chemical travelling kit is required, provided with instruments permitting the estimation of temperature, physical and

physiological properties, nitrous and nitric acids, free carbon dioxide, bicarbonate ion, native chlorine and other dissolved gases as ammoniac, oxygen etc.[151].

SPECIAL TREATMENTS.

Rare constituents may advantageously be determined by spectrographic analysis; this may necessitate the preliminary concentration of the liquid. Special sparking electrodes for working with solutions have been devised. For all chemical methods, the rare constitutents must generally be concentrated, either by *removing* most of the water and accompanying salts, or by *co-precipitation* of the rare elements with other substances. In evaporations, most of the very tedious salts may be removed by the addition of enough pure acid, e.g. hydrochloric acid for sea water, (preferably by introducing hydrochloric acid gas into the solution) or by two or three times the volume of alcohol to the liquid. In the first case, care should be taken, that co-precipitation of the constituents to be determined is not provoked by the presence of substances of similar ion radius. In the second case, this same principle may be applied profitably, to catch rare elements in precipitates of purposely added substances, (cf. p. 1—8 and an example will be found in [152], p. 567—569 and [159]). For a number of elements, other procedures have been worked out; only a few important references to recent papers can be given here [153].

METHODS OF ANALYSIS.

Only chemical methods of investigation will be treated here, for other methods and details refer to the cited manuals.

SAMPLING.

A representative sample is taken; that is, with springs, directly where the water emerges from the rock or ground, using a flask of colourless and preferably resistance glass. Artificial devices at springs make it necessary to take the sample after carefully

cleansing the outflow opening and allowing the water to flow freely for about 5'. When required, some chemical components and physico-chemical values or properties are determined *in situ*, especially the pH. 3—6 l will be required for complete investigation of the ordinary chemical constituents; the chemical estimation of rare constituents sometimes requires very large volumes [150]).

In the laboratory, a portion is filtered to remove *suspended solid matter*. This may be done through a filter crucible and the weight of the floating matter is determined, first, by sucking it completely dry, then, after drying at 105° in an oven and finally, the loss on ignition may be determined, provided a porcelain or platinum filter crucible has been used.

A known volume of the filtered sample is evaporated to determine the *salinity*, preferably using a platinum dish. The salts are dried during 1—2 hours at 180° and the weight is recorded in parts per million or in mg/l.

Water is determined exclusively by difference.

Chlorine can be determined gravimetrically or titrimetrically in 100 ml portions of the filtered sample, or in larger portions after concentration to at least 50 mg/l of Cl'. The liquid should be nearly neutral in the titrimetric determination according to MOHR; alkaline solutions are acidified with nitric acid, this solution or a primary acid sample is neutralised with excess of chlorine free magnesium oxide. Further information can be found on p. 181 and for the titrimetric determination refer to the treatises.

Sulphate is determined in 200 ml of the filtered sample. The liquid is coloured with a few drops of methyl orange solution, neutralised with 0.5 N hydrochloric acid and 1 ml of this acid is added in excess. For further procedure see p. 99 and 162.

Free carbon dioxide, bicarbonate ion, carbonate and *hydroxyl ion* are determined by titrimetric methods in 100 ml of the filtered solution. [154]) The determination of uncombined CO_2 and of HCO_3' should be done without disturbing the water; so, if possible, filtration should be omitted. I have repeatedly found rather important changes in the carbon dioxide content of irrigation water after it had passed through the pump and even after simple filtration (changes up to 4 mg/l on 6—20 mg/l) whereby the pH was changed from 7.8 to slightly more than 8.1. In most cases, the hydrogen ion concentration can be calcu-

lated from the values mentioned in this paragraph [155]), provided it is lower than 8; this will serve to check the experimental determination.

Nitrous and *nitric acids* and *ammoniac* are estimated almost exclusively with colorimetric procedures. Generally their amount is very small. [156]). Ammonia may also be determined with PREGL's (semi-) micro method, p. 184.

The determination of *phosphoric acid* is carried out in the same manner as described for the solution, obtained after the decomposition of silicates, p. 94.

The quantitative determination of *hydrogen sulphide* is scarcely worth consideration, [149e]), p. 55.

SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO are determined by exactly the same methods as have been described in the analysis of silicates. At first, the volume of liquid reserved for these operations is evaporated with hydrochloric acid in excess, to separate silica. There are, however, methods for the combined determination of CaO and MgO in terms of hardness of the water; these are often quite satisfactory for practical purposes and they work decidedly with greater rapidity. [157])

Iron may also be determined colorimetrically (titrimetric colorimetry) with a standard solution of Mohr's salt, using potassium rhodanide as a reagent. 100 ml are treated with 10 ml sulphuric acid, 1 : 5, and 3—4 ml 5 % potassium persulphate solution free from iron and boiled about 5—10' to destroy the organic matter. [158])

Manganese is determined colorimetrically after the addition of 1 % silver nitrate solution in slight excess over the quantity required for the precipitation of the known amount of chlorine ion, viz.: 6 ml 1 % $AgNO_3$ for every 100 mg Cl'/l. The silver chloride is filtered off. Proceed as described on p. 92—94.

Heavy metals are determined after preliminary concentration in suitable precipitates. Refer to cited papers. [149]), [159])

Alkalies are determined after separation of the other constituents according to a procedure which may be advantageously used also in other cases, e.g. after decompositions with hydrofluoric and other acids; this will be given in some detail. [160]) The pure CaO that is required is obtained by heating a sufficient quantity of the stock of calcium carbonate prepared for the determination according to LAWRENCE SMITH.

A quantity of the water, sufficient to yield 0.1—0.2 g of com-

bined alkali chlorides is evaporated with a small excess of sulphuric acid and the latter is expulsed by carefully heating the dry salts. The residue is moistened with hot water and transferred to a porcelain or fused silica dish. Then, freshly prepared pure CaO is added until the liquid gives an alkaline reaction on phenolphthaleine; 200 mg CaO are added in excess. The liquid is brought to boiling point and after slight cooling, the precipitated sulphates and hydroxides are filtered off and washed thoroughly with hot water.

The filtrate is treated with 1 g pure barium hydroxide and 200 mg CaO; the addition of the latter serves to avoid co-precipitation of potassium with the barium sulphate[161]). After standing overnight, the liquid is filtered and the precipitate is thoroughly washed with warm water.

To remove calcium and barium from the filtrate, a current of carbon dioxide — washed with bicarbonate solution — is introduced into the liquid until the reaction on phenolphthaleine turns acid. The bicarbonates that have formed, are converted into normal carbonates by boiling the solution until the red colour re-appears. The precipitated earth alkali carbonates are filtered off and washed thoroughly with hot water.

The filtrate is evaporated in a porcelain dish; the residue is dissolved in a few ml of water and the last traces of calcium or barium salts are filtered off after precipitation as described in the determination of alkalies in silicates and in plant ash. The further treatment, namely, weighing the combined alkali chlorides after careful neutralisation with hydrochloric acid and the separate determination of potassium or sodium is described in the sections referred to. As an alternative, the carbonates may be titrimetrically determined with standard hydrochloric acid solution, using methyl orange as an indicator[54]).

ANALYSIS OF ORE MINERALS.

The term "ore" has the same meaning here, as in current usage. The components of ore minerals chiefly belong to the first and second groups of Table I, p. 2 and so, as compared with their abundance in lower depths, they occur only in relatively minute quantities in the earth's crust. A smaller number of compounds generally reckoned as ore minerals, belong to the later stages of magmatic differentiation.

Consequently, this part of the book is divided as follows:

Siderophile :	meteoric iron	Fe, Co, Ni.
	platinum metals	Ru, Rh, Pd, Os, Ir, Pt.
	gold	Au, (Ag).
Chalcophile :	sulphides	S, Se, Te.
	(oxides)	Fe, (Co), (Ni), Cu, Zn, Cd, Pb,
	arsenic and	Sn, Ge, Mo, Ag, Hg, Ga, In, Tl.
	antimony compounds	As, Sb, Bi.
Lithophile :	oxides	Sn, W, U, Th, Nb, Ta, V, Cr, Mn.

The ore forming elements appear together in VON ANTROPOFF'S adaptation of the periodic system and are also clearly shown in a modified form according to H. S. WASHINGTON [162]).

Stress may be laid upon the importance of spectroanalytical and electrical methods of analysis (viz. electrolytic methods and potentiometric titrations), especially for series determinations in samples of this kind. In accordance with the general character of this book, only a short section dealing with electrolytical determinations is inserted. For further details refer to the manuals [163]).

ELECTROLYTICAL DETERMINATIONS. GENERAL CONSIDERATIONS.

The discharge of ions, necessary in electrolytical determinations requires an E.M.F. $= E$, characteristic for every element

and only slightly influenced by the experimental conditions. Consequently, elements may be ranged according to increasing potential difference between the element and a solution of one of its salts. The potential difference *E* may be expressed in a formula:

$$E = E_0 + \frac{R\,T}{n\,F} \ln C, \text{ or : } E = E_0 + \frac{0.0577}{n} \log C.$$

(usual symbols). When c = 1, the second term becomes zero, so, E_0 is the potential difference between an element and a solution, containing a gram-ion of the element to the liter. This is the *normal potential,* indicated in Table VII. When the concentration decreases to one tenth of its original value, E decreases with 0.0577 V for monovalent ions, with 0,0288 V for bivalent ions, with 0.0192 for trivalent ions, etc.

The normal potentials for a number of elements and radicles, of interest in this regard, are given in Table VII, [164]). The normal potential of hydrogen is arbitrarily chosen as fix point, with a value of zero, (NERNST).

Cations		↑ increasing electro-positive character	Cations		Anions	
$K/K^{\cdot}$	$= -2.92$		$Ni/Ni^{\cdot\cdot}$	$= -0.25$	$2\ F'/F_2$	$=[+2.8$
$Ca/Ca^{\cdot\cdot}$	$= -2.76$		$Sn/Sn^{\cdot\cdot}$	$= -0.14$	$2\ Cl'/Cl_2$	$= +1\ 3$
$Na/Na^{\cdot}$	$= -2.71$		$Pb/Pb^{\cdot\cdot}$	$= -0.130$	$2\ Br'/Br_2$	$= +1.0$
$Mg/Mg^{\cdot\cdot}$	$=[-2.35]$		$H_2/2H^{\cdot}$	$= 0.000$	$2\ I'/I_2$	$= +0.5$
$Al/Al^{\cdot\cdot\cdot}$	$=[-1.28]$		$Sb/Sb^{\cdot\cdot\cdot}$	$= +0.2$	$4\,OH'/O_2 + 2\,H_2O$	$= +0.4$
$Mn/Mn^{\cdot\cdot}$	$= -1.1$		$Bi/Bi^{\cdot\cdot\cdot}$	$= +0.23$	S''/S	$= -0.5$
$Zn/Zn^{\cdot\cdot}$	$= -0.76$		$Cu/Cu^{\cdot\cdot}$	$= +0.345$		
$Cr/Cr^{\cdot\cdot\cdot}$	$= -0.56$		$2Hg/Hg_2^{\cdot\cdot}$	$= +0.793$		
$Fe/Fe^{\cdot\cdot\cdot}$	$= -0.44$		$Ag/Ag^{\cdot}$	$= +0.808$		
$Cd/Cd^{\cdot\cdot}$	$= -0.40$		$Pt/Pt^{\cdot\cdot\cdot\cdot}$	$=[+0\ 86]$		
$Co/Co^{\cdot\cdot}$	$= -0.255$		$Au/Au^{\cdot\cdot\cdot}$	$= +1.38$		

Table VII. Normal Potentials. Valid for = 18°, (T = 291° K) and 1 at.

[ ] more or less uncertain.

Theoretically, an element is precipitated by the action of an E.M.F. of the calculated value and opposite sign. In practice, an

additional E.M.F. is generally required, depending on the nature of the electrode and the element in question.

It will be clear, that by electrolysis, a complete separation can never be obtained. In general practice, it is sufficient that the amount of an element remaining in the solution becomes less than 0.1 mg. E.g., from a copper salt solution, containing a gram-ion to the liter, 90 % of the metal is deposited between $E = 0.345—0.317$; 99 % between $E = 0.345—0.289$; 99.9 % between $E = 0.345—0.261$; etc. Sooner or later, the normal potential of *another* element will be surpassed; here especially As (0.3), Bi or Sb. Consequently, the completeness of electrolytic separations depends upon the circumstances.

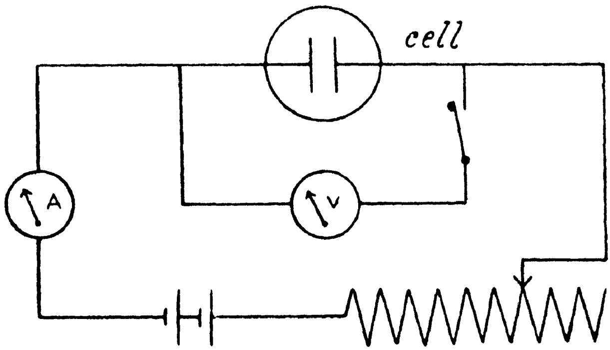

Fig. 13. Electroanalysis.

The E.M.F. required for the electrolytic decomposition of a salt solution may be calculated when the normal potentials for both ions are known; it is an additive value. For example, a normal solution of copper chloride is theoretically decomposed by the action of an E.M.F. of — (0.345—1.36) V = approx. 1 V. It is obvious that here too, an additional potential difference is required according to the nature and conditions of the electrodes and also when the concentration decreases.

The possibility of electrolytic determinations in aqueous solutions of elements with stronger electropostive character than hydrogen, depends upon these additional E.M.F., which are generally greater for hydrogen than for other elements. Often and for the same reason, it is advantageous to work with alkaline solutions.

These facts are of interest for a large number of processes in chemistry.

From the above considerations it is evident, that the adjustment of the correct E.M.F. between the connections of the cell is a *conditio sine qua non* to obtain correct results. The density of the current is also of considerable importance in view of the state of the precipitate. A too strong current causes spongeous metal layers which either, do not adhere at all, or are easily detached when the electrodes are dried. In many cases, the coatings obtained from solutions, containing the metal in complex binding, are more uniformly tight and finer crystalline — even microcrystalline — than with solutions of ordinary salts and so, the former are preferable.

To increase the rapidity of the determination, the liquid should be stirred and heated (thus promoting the adjustment of the decreasing concentration close to the cathode) and at the end, the E.M.F. may be slightly increased.

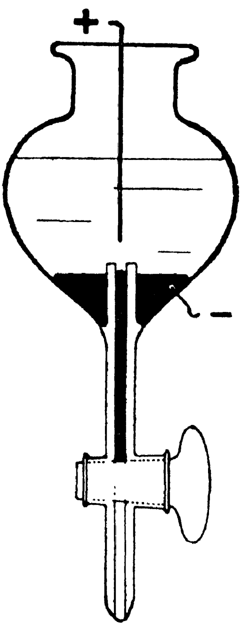

Fig. 14. Apparatus according to Cain for electrolysis with mercury cathode.

The wire gauze electrodes according to WINKLER are most convenient, except for the anodic deposition of larger amounts of lead peroxide, where sand blasted platinum dishes according to CLASSEN, with *raw* interior surface) are more appropriate. *Zinc should never be directly precipitated on platinum electrodes* as it cannot be completely removed afterwards and finally leads to the deterioriation of the expensive apparatus. First, a copper layer should be deposited to protect the electrode. Sometimes electrolysis with a mercury cathode is preferred, see fig. 14.

The stem is filled with mercury, then approx. 200 ml, exactly weighed, are placed in the cell, the solution is transferred to it and electrolysed with a current of 2—6 A, 3—7 V. The platinum wire anode should be at 1 cm over the mercury surface. The metals occurring below Zn in the electrochemical row, this element included,

are quickly removed. When the separation is considered to be complete, test with hydrogen sulphide, the stem is emptied, the electrolyte is drained off and the mercury is washed with water; only then is the current switched off. After thoroughly drying, the mercury can be weighed, the gain represents the deposited element(s). It is not feasible to recover them, as generally the mercury is impure. Proceed with the analysis of electrolyte and washings, [165]).

Like other apparatus, electrodes are treated in exactly the same way when weighed "empty" and when covered with the precipitate. The clean electrodes are washed with alcohol, finally with absolute alcohol and dried in an oven at 70—80° on a glass plate.

The electrolyte is contained in a beaker of 200 ml capacity, covered with both halfs of a clock glass, to avoid as much as possible loss of the electrolyte by sputtering, caused by the anodic evolution of oxygen. The small flame of a Bunsen burner without chimney enables heating the electrolyte at 60—70° and the liquid is effectively stirred, either mechanically, or by a rapid gas current passing through the liquid from a small opening, or electromagnetically with the ingenious apparatus described by FRARY: The beaker is placed on a hollow sheet iron body in an exact-fitting copper cylinder. The latter bears a coil, made from 120 m insulated copper wire, 1.5 mm^2 in section, total resistance approx. 1.3 Ohm. The whole apparatus is surrounded with sheet iron and requires a current of 4—6 A to yield a thorough stirring motion to the electrolyte. A separate accumulator must be used to feed the coil, as the current used for the electrolytical deposition will often be too weak. The construction will be clear from fig. 15, [166]).

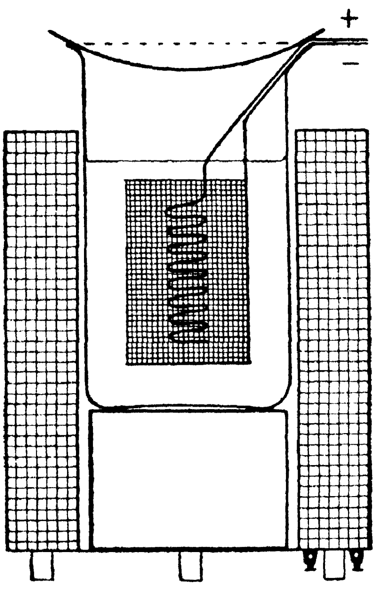

Fig. 15. Frary's apparatus for electrolysis with electromagnetical stirring.

Further details will be mentioned for the separate elements.

Analysis of Meteoric Iron. General Considerations.

Meteoric iron contains approx. 90 % iron, 7—9 % nickel, 0.5—1.0 % cobalt and minor percentages of other elements, especially copper, chromium, phosphorus, sulphur, carbon and chlorine. As the analysis of meteorites deserves much attention and the matter is also of importance in the study of artificial alloys, the methods for the examination of nickel iron alloys will be considered here.

With meteorites, great care should be taken to procure a proper sample, as free from foreign constituents (sulphide and silicate) as possible. The fragments are reduced in size on the lathe and the thin shavings are again inspected for contaminations. The sample is thoroughly freed from any oil, possibly introduced through these operations, by repeated washings (or extraction in a Soxhlet apparatus) with ether, followed by a final washing with alcohol. Then, it is dried and stored in a bottle with a tightly fitting cork, (not a rubber stopper). Sulphide parts (troïlite) and silicates are equally selected pure and reserved for separate investigation.

Analytical Behaviour of Nickel and Cobalt.

The group separations are the same for cobalt and nickel. First, the elements of the hydrogen sulphide group may be removed, or their absence tested, by introducing hydrogen sulphide into the acid solution, provided the excess of this reagent is destroyed and iron re-oxidized to the trivalent state before the addition of ammonium hydroxide, (see p. 46—47). Even considerable amounts of iron may be quantitatively separated with negligible contamination by nickel and only very slight contamination by cobalt in precipitations with ammonium hydroxide; in this case, the basic acetate method has slight advantages in view of the completeness of the separation only when considerable amounts of cobalt are present [26]. In the remaining solution, nickel and cobalt are separated electrolytically, or preferably, nickel is precipitated with diacetyldioxime (dimethylglyoxime) [167], followed by the electrolytical precipitation of cobalt. Nickel and cobalt may also be precipitated as sulphides by introducing hydrogen sulphide into the ammoniacal solution, or as carbonates

by the addition of sodium carbonate solution, containing a small quantity of sodium hydroxide, in slight excess. The precipitates obtained in the latter cases are collected on a large filter, washed with hot water and are dissolved in dilute sulphuric acid, as these precipitations are essentially preliminary separations to remove interfering substances, e.g. tartrates or large quantities of acetates. Nickel may also be precipitated with diacetyldioxime in the original solution of the sample, provided tartaric or citric acid is added, to prevent iron (aluminium) from being precipitated by ammonium hydroxyde. Small amounts of manganese are deposited as peroxide on the anode in the electrolytic determination.

ANALYSIS OF METEORIC IRON. PROCEDURE.

Approx. 0.5 g of the sample is dissolved in hydrochloric acid. When the separation of the hydrogen sulphide group is not required, the solution may be oxidized by adding a few ml of bromine water, nitric acid or hydrogen peroxide. The salts are converted to sulphates by evaporating them with sulphuric acid in slight excess. The residue is dissolved in dilute sulphuric acid and the insoluble parts are filtered off and weighed as described on p. 128. When required, they may be analysed separately.

Iron and other elements of the ammonium hydroxide group — if present — are precipitated with ammonia water in exactly the same way as described on p. 47, seq. The precipitate is dissolved in dilute sulphuric acid, re-precipitated and thoroughly washed. After dissolving again in sulphuric acid, this solution is tested with diacetyldioxime. Nickel will seldom be found. After a third precipitation, iron is determined gravimetrically as Fe_2O_3 (p. 50). Factor for Fe : 0.66946.

ELECTROLYTICAL SEPARATION OF NICKEL AND COBALT.

The electrolysis should be carried out in a strongly ammoniacal solution, otherwise hydrogen chiefly will be liberated. Nitrates retard the precipitation and therefore should be removed; with chloride and sulphate solutions equally satisfactory results can be obtained. Chromates, vanadium and tungsten are unde-

sirable, as well as organic compounds, such as acetates in large quantities and tartrates. To prepare a solution free from these interfering elements, nickel and cobalt are precipitated with a slight excess of sodium carbonate solution, containing some sodium hydroxide; the precipitates are collected on a large filter and washed with hot water. The precipitate is re-dissolved in dilute sulphuric acid. Proceed with the electrolytic determination in 100—150 ml of a solution containing 20—30 ml concentrated ammonia in excess and 5—10 g ammonium sulphate. At room temperature, with a current of 0.5—1.0 A and an E.M.F. of 3—4 V, three or four hours are required for the complete precipitation of a few tenths gram of the metals. At temperatures between 60—80°, only 100' will be sufficient. The required time may be decreased further, when the solution is effectively stirred and stronger currents are used, (30' with a current of 3—4 A). Do not prolong the electrolysis excessively, as the anode is likely to be attacked and high results are obtained. In accurate analyses, the small quantities of nickel remaining in the solution should be precipitated with hydrogen sulphide, or better still with diacetyldioxime. At the same time, this is a test for the completeness of the precipitation.

No difficulties arise when a mixture of cobalt and nickel is analysed; cobalt alone, however, is often incompletely precipitated and in a form which does not adhere to the electrode and which contains some oxide. To prevent this as much as possible, a current not higher than 0.5 A must be used and according to BILTZ-BILTZ,[168]), no troubles will occur when the FRARY apparatus is employed.

SEPARATION OF NICKEL AND COBALT. GENERAL CONSIDERATIONS.

The outstanding method of separating both metals and also at the same time the method for the quantitative determination of nickel, is the precipitation with dioxime.[167]) This procedure may be applied to the original solution of the sample, but the determination of iron and especially of cobalt will give more trouble. So, it is far better to work with the solution from which iron has been removed with ammonia as described above. Though in some cases, the presence of elements belonging to the hydrogen sulphide group will do no harm, especially when

their percentage is small, in general these should be absent. Iron, aluminium and titanium may be kept in solution by adding tartaric or citric acid in such quantities, that on the addition of ammonia, no precipitate is formed. Bivalent iron should be oxidized to the trivalent state, but any excess of the oxidizing reagent should be removed by boiling, as otherwise, the dioxime will be destroyed by it.

Cobalt may be determined in the filtrate of the nickel diacetyldioxime by electrolytic methods after destruction of the dioxime with 3 % pure hydrogen peroxide. Finally, the solution containing nickel and cobalt may be electrolysed, both metals weighed together and after dissolving in nitric acid, nickel is precipitated with dioxime and cobalt determined by difference. Consequently, this method is less preferable when only small amounts of cobalt are present. It is not feasible to work with precipitates of nickel diacetyldioxime containing more than 0.05 g Ni, as the precipitate, though being crystalline, is very voluminous. When larger amounts of nickel are in the solution, an aliquot portion may be taken, or the precipitation is carried out in the whole volume, and after thorough washing on a large qualitative filter followed by destruction of the organic reagent with hydrogen peroxide, the nickel is determined electrolytically. Unless special precautions are taken, the nickel diacetyldioxime cannot be ignited to NiO, as the precipitate is volatile at temperatures above 250°.

The volume of alcohol introduced into the solution should not exceed 50 %, as with larger percentages the nickel compound is dissolved. The excess of reagent should be as small as possible, as through the dilution with the test solution, a precipitate of diacetyldioxime may be formed, thus leading to plus errors in the determination of nickel. When considerable quantities of cobalt, manganese and zinc are present, the excess may be larger, as these metals also require the reagent to form soluble compounds. In this case it is far better, to make the solution very faintly acid and after heating to boiling point, the required quantity of the reagent is poured in, followed by a concentrated solution of sodium acetate until the precipitate has completely formed; then, 1—2 g of the salt are added in excess.

PRECIPITATION OF NICKEL DIACETYLDIOXIME. PROCEDURE.

A 1 % alcoholic solution of diacetyldioxime is used. 4 ml are theoretically required to precipitate 0.01 g Ni and an excess of not more than 25 %, viz. in total 5 ml for every cg of Ni may be used.

The solution is heated to boiling point and when made ammoniacal, no precipitate should appear, otherwise tartaric acid should be added. Dilute hydrochloric acid is added until the solution is slightly acid, the volume is made up to 150—200 ml, the temperature should be 70—80°. The required amount of reagent is added, directly followed by dilute ammonium hydroxide until the precipitation is complete; a very slight excess of ammonia should be present at the end. The beaker is kept hot on the water-bath for an hour, then the precipitate is filtered off in a glass or porcelain filter crucible, washed with hot water, drained well, and dried completely at 110—120° in an oven.

The composition of the precipitate is $NiC_8H_{14}O_4N_4$.

Factor for NiO : 0.25873.

for Ni : 0.20331.

When the volume of the precipitate is too large, to be conveniently handled in a filter crucible, the filtration should be done with a large paper filter. After thorough washing with hot water, the precipitate is transferred to a 200 ml beaker and boiled with 10—20 ml 3 % pure hydrogen peroxide. After complete destruction of the dioxime, ammonia and ammonium sulphate are added and the solution is electrolysed as described above.

ELECTROLYTIC DETERMINATION OF COBALT. PROCEDURE.

Cobalt is determined in the filtrate from the determination of nickel with dioxime after destruction of the organic matter as described above. This will probably not represent all the cobalt in the sample, as this metal is retained in the ammonia precipitate slightly more than nickel. Generally this will not necessitate the application of the basic acetate method as only some 2 % of the total amount of cobalt is lost and cobalt is less abundant than nickel.

ANALYSIS OF TECHNICAL IRON AND STEEL. GENERAL CONSIDERATIONS.

Technical iron contains variable quantities of other elements and these largely influence the properties of the product. The most common among them are: C : 0—7%, Si : O.OX %, but much more in ferrosilicon, P : O.OX—2 %, Mn up to 80 % in ferromanganese, but generally not more than 4 %, Cu : 0—0.2 %, Ni up to 10 %, Cr up to 18 %, vanadium is also used more and more.

For the preparation of the sample, cf. the foregoing section.

Iron is generally present in quantities of more than 90—95 % and in this case is reported exclusively by difference. Short indications are given for the determination of other constituents.

Nickel and *cobalt* are determined as in meteoric iron. Mere traces of cobalt are present in most cases.

Copper is determined as oxide after a precipitation with hydrogen sulphide in the solution obtained after the determination of sulphur. A purification by fusion with potassium pyrosulphate, followed by filtration, is required to remove traces of silica which remain either undissolved, or in a colloidal form in the decomposition. Copper is re-precipitated as sulphide, or electrolytically.

Chromium and *manganese* are determined according to titrimetric methods, refer to manuals on this subject.[169]) In the estimation of manganese according to the bismuthate method, cobalt interferes and must be removed beforehand. Sometimes a decomposition with sodium peroxide, as prescribed for the analysis of chromite, p. 230, should be applied on the finely divided sample, as high grade chromium steels resist acid attack.

Silicon and *tungsten* are determined in 2—1 g of the sample. this is dissolved in nitric acid and evaporated to dryness, followed by repeated evaporations with hydrochloric acid. Alternatively, it has been recommended to use perchloric acid, followed by boiling with dilute hydrochloric acid.[170]) When graphite is present, the filtered silica should be heated over a powerful blast to oxidize the carbon. This is inconsistent with an accurate determination of tungsten which is volatilized at temperatures higher than 850°. Fortunately, both constituents rarely occur together. Silica is determined by difference after volatilization with hydrofluoric acid, see p. 44, seq. A yellow residue from this evaporation is counted as WO_3. Factor for W : 0.79321.

Sulphur is determined according to JÄRVINEN as barium sulphate after decomposing a sufficient quantity (5 g) of the sample with an excess of sulphur free bromine, (8—9 ml), in 100 ml water.[171] After complete decomposition of the shavings, the excess of bromine is removed by boiling. Sulphur is precipitated in the cooled liquid with 30 ml of a cold saturated solution of barium chloride. After standing a few hours, the impure barium sulphate is filtered off, fused with an excess of sodium carbonate and treated further as described on p. 99 and 162.

Sulphur may also conveniently be determined according to SCHULTE by absorbing the hydrogen sulphide, formed when the sample is dissolved in hydrochloric acid, in cadmium acetate solution.[172] After double decomposition with copper sulphate solution, the precipitated copper II-sulphide is filtered off and ignited. The amount of sulphur present in the sample is calculated on this basis. For a complete description see BILTZ-BILTZ[173], p. 271 seq.

Phosphorus is determined as phosphomolybdate, see p. 95. Silicon should be completely removed as it interferes with this determination. 2 g of the sample, but 1 g if much phosphorus is present is dissolved in nitric acid, 1 : 1, in a small pyrex beaker. After the decomposition, transfer the solution to a small platinum basin and boil with 1 ml of hydrofluoric acid. The further treatment as described in the section referred to. Factor for P : 0.01654.

PLATINUM METALS AND GOLD.

The platinum metals and gold are generally determined according to docimastic or micro-docimastic methods. A few references from outstanding and recent literature on this subject are given, as a description of these methods goes far beyond the scope of this book[174]. The micro-docimastic methods[175] have proved indispensable in the investigation of a number of problems in geochemistry.

ANALYSIS OF SULPHIDES, ARSENIDES AND ANTIMONIDES. GENERAL CONSIDERATIONS.

These substances generally occur combined in nature, though

sometimes, sulphides are found alone. To be able to devise the scheme of the analysis, the knowledge of the qualitative composition of the sample is absolutely necessary. For this matter refer to the considerations on p. 5, seq. Blowpipe methods are excellent to determine minerals of this kind.

The determination of the non-metallic elements is considered first, as, either the remaining solutions may often advantageously be used for the determination of the metals, or the decomposition for this part of the analysis is made according to analogous principles. Further, tin is generally treated together with arsenic and antimony as the methods of separation for these three elements are closely related. Compounds, containing tin or antimony require a special treatment, owing to the hydrolysis these elements undergo in solutions.

Alloys, except special light alloys, are mainly composed of elements, dealt with in these sections, as indeed, sulphidic ores are our chief sources of many important metals. Consequently, after suitable decomposition, these alloys can be analysed according to the same methods, so that a few considerations regarding these substances are made. The methods for the analysis of alloys, exclusively composed of light metals will be found in foregoing chapters and finally, in the investigation of alloys containing heavy as well as light metals, the separation of both groups will generally not give excessive difficulties.

SULPHIDES. GENERAL CONSIDERATIONS.

Except when especially mentioned, sulphides should not be too finely pulverized in the preparation of the sample, as marked oxidation is the result: some of the sulphur escapes as dioxide, whilst another part is oxidized to sulphate. In determinations of sulphur, care should be taken throughout, *to avoid contamination by flame gases,* protecting the fusions and solutions with screens or by working with alcohol burners or electrical heating apparatus.

Sulphur is almost always determined as sulphate after preliminary oxidation, see however the procedure of SCHULTE, mentioned on p. 206, whilst minute percentages of H_2S are often colorimetrically determined by comparing the stain, produced on paper drenched in cadmium acetate solution, with a colour scale.

The oxidation to sulphate is obtained according to one of the following methods: 1. Fusion with sodium carbonate and nitre, or sodium carbonate and chlorate, or sodium peroxide. 2. Decomposition with a mixture of HCl and HNO_3, either concentrated, or dilute. 3. Decomposition in a current of chlorine or bromine, or with liquid bromine. 4. Thermal decomposition of the sample; the liberated sulphur dioxide is absorbed in a mixture of ammonia and hydrogen peroxide to oxidize it to sulphuric acid and to absorb it as ammonium sulphate.

DETERMINATION OF SULPHUR. PROCEDURES.

These methods will be subsequently considered. The method of decomposition in a current of chlorine or bromine, however, will be mentioned in a further section as it is valuable especially to separate arsenic, antimony and tin at the same time.

1. In the classical procedure of R. FRESENIUS [176]), the sample is finely pulverized, (preferably under alcohol, as advocated by HILLEBRAND for the determination of ferrous iron) and heated with 8—10 g of a mixture of sodium carbonate and *sodium* nitrate, 3 : 2. [177]) Care should be taken to use reagents and apparatus as free from sulphur as possible. The procedure of the fusion is essentially the same as described on p. 99. The quantity of sulphur in the sample should not exceed 0.1, at most 0.15 g. This is mixed thoroughly with 6 g of the flux, transferred to the crucible and covered with the remaining part of the mixture. The temperature is gradually raised to avoid a too strong reaction. After complete cooling, the crucible is placed in a beaker with water. The melt disintegrates and the solution is treated with a few drops of alcohol to reduce manganates. To precipitate lead and zinc, which will have been partly dissolved, a current of pure carbon dioxide is introduced for about 30'. The gas should be washed with copper sulphate solution and water to retain traces of hydrogen sulphide, or a cylinder with the liquefied gas can be used. Then, the liquid is boiled to remove carbon dioxide and to destroy soluble bicarbonates. After filtration, the undissolved parts are adequately washed with a hot dilute (2 %) solution of sodium carbonate and finally with water. The filtrate is acidified with HCl, evaporated to dryness and this is repeated with 10 ml of concentrated HCl. The salts are treated

with just enough concentrated HCl to moisten them and dissolved in a minimum volume of water. The filtered solution, now free from silica is diluted to 300 ml in a 600 ml beaker, heated to boiling point and a small excess of 1 % hot barium chloride solution (70 ml for 0.1 g of S) is added at one pouring. The co-precipitation of barium chloride counterbalances the error due to the co-precipitation of alkali sulphate. The further treatment as described on p. 162, seq. Factor for S : 0.13730.

The nitrates need not be destroyed when the sample is fused with 50 times the weight of a mixture of sodium carbonate and sodium chlorate. (The sodium salt should be used instead of the recommended potassium chlorate to prevent excessive contamination of the barium sulphate by potassium.) The fused cake is extracted with water as above and the filtrate is acidified with hydrochloric acid. The liquid is evaporated to complete dryness; then the salts are moistened with conc. HCl and dissolved in water. The further treatment as described above.

Instead of these mixtures, 5—10 g of sodium peroxide may be used as a flux. The finely pulverized sample is mixed with sodium peroxide and as much sodium carbonate that explosions need not be feared. The relative quantities to be taken depend upon the nature of the sample, this should be previously tested. An iron crucible is used. The temperature is gradually raised to avoid too violent reaction. When the contents of the crucible are just fused, the decomposition will soon be complete. After cooling, the crucible is placed in a small beaker with a cover, to avoid loss by spluttering and water is added. Oxygen is liberated as the melt dissolves. The liquid is treated as described above. It is obvious that an *additional* evaporation with hydrochloric acid is not required as nitrates are absent.

2. The liquid attack yields the amount of *sulphide* sulphur but only when not more than small quantities of lead are present [178]). This, however, is the amount of sulphur available in the technical decomposition for the sulphuric acid industry. Consequently, this procedure is almost universally adopted in the analysis of pyrites for this purpose.

0.5 g of the finely pulverized sample is treated in a covered porcelain dish with 10 ml of mixed concentrated nitric and hydrochloric acids, 3 : 1. In general it is unnecessary to heat, often a violent reaction requires even tempering by cooling. After standing overnight, the dish is heated on the water-bath;

no sulphur should appear, otherwise the decomposition must be repeated with more concentrated HCl and gentler attack at the beginning. The residue is moistened with 5 ml conc. HCl and again evaporated to dryness. The chlorides are moistened with HCl and dissolved in water, insoluble parts are filtered off and in the filtrate, sulphur is determined according to one of the methods prescribed on p. 162, seq., for the presence of much iron.

A far better and more convenient decomposition may be obtained according to ALLEN and JOHNSTON by heating 0.5 g of the sample with 4 ml of fuming nitric acid in a sealed tube at 120—130° overnight. [179]) The sample is weighed out in a small thin-walled tube made from a test tube. The use of sulphur free glasses is imperative, as I often observed marked attack. The acid is poured into the bomb tube and the sample is carefully introduced. Generally the light tube will stick to a wet part of the wall of the heavy tube, thus avoiding untimely attack. The further procedure is essentially the same as described above, viz. evaporation with hydrochloric acid, etc.

According to JÄRVINEN [180]), a mixture of concentrated nitric and hydrochloric acids and water, 2 : 1 : 7, is prepared. 0.5 g of the sample is treated for about 30' in an Erlemeyer flask of 300 ml capacity on the water-bath with 10—15 ml of this mixture. A trap for escaping volatile sulphur compounds is used, consisting of a stopper fitted with a U-tube, containing bromine water. After almost complete decomposition, the flask is cooled and 1 ml of pure distilled bromine is added to the contents, 15' later, 2 ml of ether and after another 15', the contents of the trap. Then, the ether and the excess of bromine are removed on the water-bath. Silica and insoluble matter are separated as described above. In the original description of JÄRVINEN, co-precipitation of iron is avoided by reduction with hydroxylamine chloride. Any of the other described methods may be used with equal profit and without much more time being spent.

The same procedure may be employed to decompose elementary sulphur. 0.1—0.2 g of the finely powdered sample is treated with 30 ml water and 2 ml pure bromine as described above. When all the sulphur has reacted with the bromine, 5 ml ether are added and after half an hour, the reagents are volatilized at as low a temperature as possible, to prevent loss of bromine

sulphur. The precipitation has been described on p. 162. Barium chloride solution should be added dropwise to the hot liquid in very small excess.

4. For the description of this procedure, refer to Biltz-Biltz, [181]), p. 292. The sulphur oxides are absorbed in a mixture of 3 % ammonia and 3 % hydrogen peroxide or in standard sodium hydroxide solution with *neutral* peroxide. Sulphuric acid is determined in this liquid, either titrimetrically, oi gravimetrically. This method seems to be excellent for industrial purposes and when a permanent apparatus is available; the author has had no experience with it and the method is not recommended for occasional determinations. Alternatively, the same end may be reached by a decomposition with hydrochloric acid; the liberated hydrogen sulphide is caught in the same absorption liquid and retained as sulphate.

DETERMINATION OF SELENIUM AND TELLURIUM. GENERAL CONSIDERATIONS.

Both elements are found in rare occurrences, often together with comparable sulphur compounds. For the determination of minute percentages of selenium cf. [182]). The chlorides of both elements are easily volatile and hydrochloric acid solutions should not be heated unless when weaker than 6 N and not at higher temperatures than 100°. The sample may be decomposed by oxidizing fusions, viz. with soda and nitre in a porcelain crucible or with sodium peroxide in a nickel crucible, or by heating at 500° in a current of chlorine; then, the volatile products are caught in dilute hydrochloric acid. In the former cases, the fused cake is extracted with water and after filtration, the liquid is acidified with HCl and heated at 90° to convert selenium and tellurium from the sexivalent to the quadrivalent state. In the absence of nitric acid, the quadrivalent compounds are reduced to the elements by sulphurous acid. The solution should be 3.4—5 N of hydrochloric acid. Interfering elements will not be present after oxidizing fusions. Complete separation of selenium *without* tellurium can be obtained in cold hydrochloric solution, stronger than approx. 9 N. Tellurium may be determined by difference, or according to special methods in the filtrate from the precipitated selenium. With regard to the rareness of tellurium, a reference to the literature is given. [183])

PROCEDURE FOR THE DETERMINATION OF SELENIUM.

To not more than 0.25 g of each element in 100 ml of a cold concentrated hydrochloric acid solution is added 50 ml saturated sulphur dioxide solution in concentrated HCl. After the precipitated red selenium has collected on the bottom of the beaker, the liquid is filtered off through a porcelain filter crucible. Wash adequately with cold conc. HCl, then with water, alcohol and ether in this order. Dry at 35° for 3—4 hours to remove the ether and at 120° for another two hours to completely dry the precipitate; weigh as Se.

DECOMPOSITION OF ARSENIC, ANTIMONY AND TIN MINERALS.

Trivalent arsenic is much more volatile than quinquevalent, consequently, in the decomposition an oxidizing attack should be used to catch all the arsenic. A method of determination of both forms can also be based on this conduct.

The outstanding methods of decomposition are: 1. heating with sulphuric acid, 2. fusion with alkali carbonate and sulphur, 3. thermal decomposition in a current of chlorine or bromine.

1. Approx. 1 g of the sample is weighed out and heated with 15 ml of concentrated sulphuric acid in a Kjeldahl flask of 100 ml capacity [184]). In most cases, 15' are sufficient to completely dissolve the mineral. Copper, cobalt and nickel compounds must be finely divided, substances consisting essentially of non metallic elements, however, yield easily to attack. When sulphurric acid alone is insufficient, the sample is first digested with nitric acid. 15' are required to decompose the sample and to remove nitroso vapours and a large part of the nitric acid, this however, is essential, especially when titrimetric procedures for the determination of As and Sb are applied in connection with the distillation method. After cooling, 15 ml concentrated sulphuric acid is added and the flask is again heated to completely remove the nitric acid and a large part of the sulphuric acid; approx. 4 ml of the latter should remain. In the case of elementary sulphur being liberated in the decomposition flask, the whole apparatus is gently heated by waving with a flame until all the sulphur is removed. After cooling, the liquid is diluted with 100 ml water in the vessel reserved for the further treat-

ment. If antimony or tin hydroxides are separated, enough hydrochloric acid is added to dissolve these.

2. In the decomposition by fusion with anhydrous alkali carbonate and sulphur (often called "Freiberger method"), the active reagent is alkali polysulphide, formed during the decomposition [185]. Consequently, when the fused cake is dissolved, at the same time a separation of arsenic, antimony and tin from other elements is effected, this being one of the greatest advantages of the method.

The relative quantities of anhydrous carbonate and sulphur are chosen so as to yield approximately the trisulphides, as these are most resistant to higher temperatures and are formed even with a larger excess of sulphur. With *soda* and sulphur, a 1 : 1 mixture is generally used, with *potash*, 4 parts of sulphur to 5 parts of carbonate may be taken. Only purified sulphur should be used for this attack [186]. Most substances, even alloys, are easily decomposed by the flux. Otherwise a preliminary treatment with nitric acid should be applied.

1 g of the sample is weighed out and is thoroughly mixed with 6—8 parts of the flux, adequately mixed itself. The mass is placed in a thick-walled porcelain crucible and should not occupy more than half the available room. The mixture is covered with more flux, until the crucible is filled to two thirds of its height. The crucible is covered and very gently heated at first; gradually the temperature is raised. Too quick heating at higher temperatures removes most of the sulphur before reaction with the carbonate can take place. After complete reaction of the flux (15—20' are required), the full heat of a Meker burner is applied to sulphurize the sample and to convert the metallic sulphides in a crystalline form in which they are easily filtered off. After another 15' the heat is *gradually* decreased, otherwise the crucible is likely to crack; for the same reason, the crucible should have rather thick walls.

The contents are digested with approx. 100 ml hot water in portions; the sulphosalts of arsenic, antimony and tin are dissolved, sulphides of other elements remain in an easily filterable form. Occasionally, the presence of iron causes a dark green colour in the solution, owing to colloidal dissolved iron sulphide. In this case, potassium carbonate should be used for the decomposition, when necessary, a few grams of solid potassium chloride are added and the liquid is digested on the water-bath to

salt out the iron. Finally, the solution should have a golden yellow to brownish yellow colour tone and be perfectly clear. The residue is filtered off and washed with 2 % sodium sulphide solution (when iron is present, add some potassium chloride to the wash liquid) and with hot water after the beaker under the filter has been substituted for a new one. Copper is often dissolved somewhat; this may be corrected by gradually adding potassium cyanide to the warm solution (60—70°), before acidifying, until the liquid is only faintly yellow. Polysulphide sulphur is bound as rhodanide. Allow to stand overnight in a warm place. At the same time, this is an effective way to avoid co-precipitation of excessive amounts of sulphur on acidifying the solution. The latter operation should be carried out under a hood with vigorous draft. (Possibility of HCN).

The filtrate is acidified by adding dropwise hydrochloric acid to the solution. The sulphides of arsenic, antimony and tin are precipitated. The beaker is covered and allowed to stand overnight, then the mixed sulphides are filtered off.

3. The third method of attack to be mentioned here separates arsenic, antimony, tin and other elements yielding volatile chlorides or bromides [187]). The attack is often used for complex substances like fahlores, especially when these are rich in bismuth and mercury, for some nickel ores and when selenium is present. The decomposition should be started at as low a temperature as possible with a perfect dry portion of the sample and dry apparatus to prevent hydrolysis. The volatilized chlorides are absorbed in dilute hydrochloric acid and the tube serving in the decomposition is rinsed with the same liquid after the attack. S, As, Sb, Sn, Hg, Bi and Se are volatilized; iron and zinc divide. For particulars refer to the cited papers.

METHODS OF SEPARATION FOR ARSENIC, ANTIMONY AND TIN. GENERAL CONSIDERATIONS.

After a "Freiberger" decomposition, a separation of the above elements from all others has been obtained, as described. After other methods of decomposition, a preliminary separation with hydrogen sulphide should be followed by some process more or less equivalent to the sulphurizing decomposition, viz. digestion with alkali polysulphide solution. The three above elements

mutually, can be separated, either according to precipitation processes, or with fractional distillations, or they may be estimated by volumetric methods. After strong oxidizing attacks, e.g. with nitric acid, arsenic is present in the quinquevalent condition. In this case it is advisable to apply the distillation methods directly on the liquid obtained in the decomposition. In the following sections these operations will be considered.

PRECIPITATION WITH HYDROGEN SULPHIDE IN STRONG ACID SOLUTION.

Both the copper group and the arsenic group are precipitated. The former includes the elements: Ag, Hg, Pb, Cu, Bi, Cd, Ru, Rh, Pd, Os, (Tl, In, Ga.); the arsenic group includes: As, Sb, Sn, Au, Pt, Ir, Ge, Se, Te, Mo, (V, W.). Those elements placed in brackets are incompletely precipitated and not at all in the presence of tartaric acid.

Procedure. Prepare a hydrochloric or sulphuric acid solution free from excessive amounts of nitric acid (less than 3 %). The exact amount of acid is not largely of influence, but to avoid as much as possible the co-precipitation of elements belonging to the ammonium sulphide group, or rather of the transitional elements between both groups (zinc, cobalt and nickel), it is best to begin the precipitation in a stronger acid medium than is finally required, adjusting the correct acidity by diluting with water when most of the elements of the hydrogen sulphide group have been precipitated and contamination is less to be feared. Solutions with a final concentration of 1 % HCl, or 0.5 % sulphuric acid by volume are suitable; the latter serve better for precipitations of platinum and molybdenum. Wash the precipitate with a solution of the same composition, viz. with acidified hydrogen sulphide water and prevent as much as possible oxidation of the precipitate by covering the funnel with a watch glass and not allowing the precipitate to drain completely.

SEPARATION OF ARSENIC, ANTIMONY AND TIN FROM OTHER ELEMENTS.

Precipitate with hydrogen sulphide as described above. The mixed sulphides are washed with as small a volume of water as feasible in a beaker, which is then placed under the funnel. The

filter paper is washed with a concentrated sodium sulphide solution containing some sulphur. Use ammonium polysulphide only when mercury is present, as copper is likely to be dissolved more or less in this reagent. The sulphides in the beaker are digested with the alkali poly-sulphide solution on the water-bath and filtered off on the original filter.

The filtrate is only just acidified to precipitate the sulphides of the three elements.

SEPARATION OF ARSENIC, ANTIMONY AND TIN. PROCEDURES.

Innumerable methods have been worked out for the separation of these elements. All of them suffer from minute imperfections. The complete description of one scheme is given and a few references to the original literature.

The three elements may be subsequently distilled under well defined conditions and each of them estimated separately in the distillate. Many workers have improved these methods [188]). A comparatively simple determination is that, in which arsenic is distilled off from a hydrochloric acid solution after reduction to the trivalent state by hydrazine sulphate, sulphur dioxide, hydroiodic acid or hydrobromic acid. A distillation apparatus as represented in fig. 12 a and b, p. 184 is suitable, provided more holes in the stopper permit the introduction of a thermometer and inlet tube in the decomposition flask. The thermometer extends to within 3 of 4 cm of the surface. The rubber stoppers and connections should be free from antimony as this element yields the same reactions as arsenic and when qualitatively detected in the distillate, its presence might suggest incorrect conditions of distillation. The temperature of the vapour should not be allowed to exceed 107—108°, otherwise antimony will be partly volatilized. Small amounts of arsenic can be quantitatively distilled without the aid of a gas current. (fig. 12 a.) When greater amounts are present, it is better to use an apparatus as represented in fig. 12b. Hydrochloric acid gas is generated in *G*. In this case it is advisable to protect the absorbing apparatus with a trap to prevent loss of arsenic when a rapid gas current is maintained.

Precipitated sulphides are prepared for the distillation by dissolving them in ammoniacal hydrogen peroxide; the liquid ob-

tained in an acid decomposition may be directly used, provided nitric acid is quantitatively removed and not more than 4 ml sulphuric acid are present. 200 ml hydrochloric acid are added and to reduce the arsenic to the trivalent state, 1.5 g hydrazine sulphate or 20 g ferrous sulphate or a few ml hydrobromic or hydroiodic acid are required. The volume of the liquid should not be allowed to become less than 30—40 ml. It is advisable to repeat the distillation with a fresh supply of 50 ml hydrochloric acid. Arsenic is determined in the distillate according to one of the methods described in a further section.

When a mixture of trivalent and quinquevalent arsenic is heated with sulphuric and hydrofluoric acids, trivalent arsenic is volatilized, whilst quinquevalent arsenic is retained in the liquid. After a separation of trivalent arsenic by this procedure, quinquevalent arsenic may be determined according to one of the available methods. This percentage, subtracted from total arsenic yields the amount occurring in the trivalent condition.

The described separations are especially valuable when tin is absent or has been removed by the following procedure:

SEPARATION OF TIN FROM ARSENIC AND ANTIMONY. PROCEDURE.

When the three elements are present as sulphides, these are mixed with 2 g of pure sulphur and dissolved in a few ml of concentrated sulphuric acid by heating in a platinum or fused silica dish. Dilute with 100 ml water, filter to remove the excess of sulphur and catch the filtrate preferably in a platinum basin, or else in a Pyrex beaker. A few ml of hydrofluoric acid are added to this solution, or to any other acid solution of the same composition. A treatment with hydrogen sulphide then causes only the separation of arsenic and antimony.

Tin is determined in the filtrate by precipitation with cupferron [189]). Hydrogen sulphide is removed from the solution by boiling, then, 3—4 g solid boric acid [190]), some 5 ml concentrated sulphuric acid, 5—10 ml concentrated hydrochloric acid and an excess of a 10 % cold cupferron solution in water are added, whilst constantly stirring until the precipitate becomes compact. As this will last approx. half an hour, the use of a mechanical stirrer is recommended. The precipitate is filtered off, washed with cold water and after drying, it is carefully ignited. Weigh as stannic oxide. Factor for Sn : 0.78766.

SEPARATION OF ARSENIC FROM ANTIMONY. GRAVIMETRIC DETERMINATION OF ARSENIC.

Arsenic can be precipitated: 1. as magnesium ammonium arsenate and 2. as silver arsenate. For both methods the oxidation to the quinquevalent condition is required. This may best be obtained by nearly neutralising the free acid in the solution with ammonia, heating to boiling point and oxidizing with 6 g of solid potassium persulphate in small portions. Sulphides are prepared for this treatment by heating them with a few ml ot fuming nitric acid in a platinum dish, evaporating the solution almost to dryness, followed by the addition of 2 ml hydrofluoric acid and 100 ml water. The presence of hydrofluoric acid promotes the dissolution of antimony.

1. *Determination of Arsenic as Magnesium Ammonium Arsenate* [191]) is carried out according to the same principles as the determination of phosphorus as magnesium ammonium phosphate, p. 144 and 169. 15—20 ml ammoniacal magnesium mixture are added dropwise to the cold concentrated solution whilst constantly stirring. Then, 20 ml concentrated ammonium hydroxide is added and the liquid is allowed to stand overnight or 24 hours. Double precipitations are always required to avoid contamination, especially by sulphate and potassium. So, the liquid is *decanted* through a small filter; the minute quantity of the precipitate on the paper is washed with warm dilute nitric acid, 1 : 3, and this liquid is caught in the original beaker. The paper filter is washed with very dilute nitric acid, 1 : 99. After the addition of 1 ml magnesia mixture, the precipitation is repeated with ammonia, using phenolphthaleine as an indicator as described for the determination of P and Mg on p. 69 and 169.

The precipitate is collected in a porcelain filter crucible and sparely washed with 5 % ammonium nitrate. Gradually heat and weigh as $Mg_2As_2O_7$. Factor for As : 0.48259.

A paper filter cannot be used, as the precipitate is reduced by charring paper. Antimony should be kept in solution by adding 10 times the stoichiometric amount of tartaric acid, say a few tenth's of a gram.

2. After the same preliminary treatment, viz. separation of tin and oxidation to the quinquevalent condition as described above, *arsenic may be determined as silver arsenate* [192]). Chlo-

rides should be absent. The oxidized solution is transferred to a platinum or fused silica dish, 15 ml concentrated sulphuric acid are added and the liquid is evaporated until heavy fumes of sulphuric acid are liberated. After cooling, the solution is diluted to 100 ml with water and a few drops of methyl orange solution are added. The liquid is neutralized with concentrated ammonia until the colour changes and heated to boiling point. Add silver nitrate in slight excess and stir vigorously. The clear supernatant liquid is tested with litmus paper and should be faintly alkaline, otherwise dilute ammonia is added drop by drop until the reaction turns alkaline.

After cooling, the silver arsenate is filtered off by means of a porcelain filter crucible and is washed with five 10 ml portions of cold water, containing 5 g ammonium nitrate and 0.25 g silver nitrate to the liter. Finally, wash with a few ml alcohol. Dry and heat to approx. 500° in an electric oven or in an hot air bath, not over the free flame lest the precipitate is reduced. Weigh as Ag_3AsO_4. Factor for As : 0.16194.

The precipitate may also conveniently be determined titrimetrically [193]. Antimony is determined in the filtrate as follows:

DETERMINATION OF ANTIMONY.

The filtrate and washings from the silver arsenate or the magnesium ammonium arsenate are used. In the former case, the alcoholic washings are not required and silver should be removed by a minimum volume of dilute hydrochloric acid.

The filtered liquid is heated to fumes with 10 ml concentrated sulphuric acid and antimony is reduced to the trivalent state by boiling this liquid with 2 g of pure sulphur. After cooling and dilution with water, the excess of sulphur is filtered off. Antimony can be determined gravimetrically as trisulphide or as tetroxide [194]. In this case, however, it is much more convenient to determine the metal volumetrically by oxidation with potassium permanganate in presence of hydrochloric acid [195]. Per 100 ml of solution, 10 ml sulphuric acid should be present and 10—25 ml concentrated hydrochloric acid. The solution is titrated with standard permanganate solution at 10° until a faint pink colour lasts 5". Calculate on the basis of oxidation from Sb_2O_3 to Sb_2O_5, or with an experimentally determined factor, after

standardization of the permanganate solution with a knowr amount of antimony, dissolved in sulphuric acid and treated a: described above.

When a gravimetric determination is preferred, the antimon III-sulphide is filtered in a porcelain filter crucible, previousl dried at 280°. Sulphur is removed by drying the crucible fo about 2 hours at 120° followed by heating for another 2 hour at 280—300°. The whole operation should be carried out in carbon dioxide atmosphere free from oxygen to avoid oxidatio of the sulphide. Weigh as Sb_2S_3. Factor for Sb : 0.71695.

METALLIC ELEMENTS IN ORES. GENERAL CONSIDERATIONS.

The following metallic elements occur in natural minerals o ore character: Ag, Hg, Pb, Bi, Cu, Cd, Mo, Fe, Ni, Co, Zn, (As Sb, Sn). Their determination in minerals is considered in th following sections.

Silver, when present in minute percentages, should be esti mated according to docimastic methods, for larger quantitie the gravimetrical determination as silver halide is entirely sa tisfactory.

Mercury is generally determined in a separate portion accor ding to special methods. It does not interfere in analyses fo other constituents owing to the volatility of its compounds.

Bismuth is determined as Bi_2O_3 after hydrolysis of a feebl acid solution, or after precipitation with ammonium carbonat in nearly neutral solution.

Lead, when present in small amounts, is best determined b electrolytical deposition as peroxide on the anode. Large amounts should be precipitated and weighed as sulphate.

Copper may be determined gravimetrically as Cu_2S or CuCNS or preferably by electrolysis as metallic copper.

Cadmium is precipitated as sulphide and weighed as sulphat after the electrolytical determination of copper. A descriptio of this procedure has been given on p. 155. As an alternative, th electrolytic determination is given.

Molybdenum is determined in a separate portion of th sample. Generally the percentage of this metal in sulphides i so low that its influence on the determination of other element can be neglected.

Zinc is determined in the filtrate from the hydrogen sulphide group s.s. In a *feebly* acid solution, it is precipitated by H_2S and weighed after conversion into sulphate as described on p. 155. Alternatively, zinc may be precipitated by electrolysis.

Iron, cobalt and *nickel* are determined in the filtrate from the above group according to the methods described in the section on the analysis of meteoric iron.

The scheme for the analysis of a sample containing these metals may be sketched as follows:

After suitable decomposition, silver is precipitated as chloride. The hydrogen sulphide group is precipitated as described on p. 215 and when necessary, the sulpho salt forming elements are removed by a treatment with alkali polysulphide. (Mercury), bismuth, lead, copper and cadmium remain undissolved; these metals are separated according to the above principles. In special cases a shorter scheme may lead to the same end.

DETERMINATION OF SILVER. GENERAL CONSIDERATIONS.

Silver is present in many sulphidic ores in minor quantities and for a larger percentage in fahlores. Further it occurs native and as the halide. For the decomposition of halogen minerals containing silver, see p. 176; it is obvious that in this case, the silver regulus should be dissolved in nitric acid. In ores, silver is generally determined according to docimastic methods, thus following the technical process where silver is concentrated in the lead phase. Silver is then determined after oxidation of the lead. The gravimetric process of determination as silver halide, further, titrimetric procedures [196]) are likewise very suitable.

The most favourable conditions for the *gravimetric process* have been enumerated on p. 181. The errors are negligible, provided proper care is taken to avoid co-precipitation of other substances. After an attack by oxidizing fusion, the elements which are likely to influence the determination of silver are: lead, bismuth and antimony. Lead can be completely separated, either as sulphate before the precipitation of silver, or by precipitating silver chloride in dilute solutions. If necessary, the precipitate is dissolved in ammonia, filtered and re-precipitated by the addition of nitric acid. This is also a convenient method

of purification in other cases, e.g. bismuth. Finally, the precipitated impure silver chloride may be treated as prescribed on p. 176 for the natural silver chloride.

DETERMINATION OF SILVER. PROCEDURE.

Prepare a solution of silver nitrate in 1 % nitric acid and as free from other substances as possible. This solution should be diluted with water containing 1 % of nitric acid until not more than 0.1 g Ag is present per 200 ml of liquid. Precipitate with a small excess of dilute hydrochloric acid, added drop by drop whilst constantly stirring. By this strong motion the precipitate settles within a short time when chlorine and silver are present approx. in equivalent amounts, so that the completeness of the precipitation can be easily tested. Allow the precipitate to stand overnight in a place where it is protected against direct daylight or strong artificial light sources. The supernatant liquid is decanted through a porcelain or glass filter crucible and the precipitate is washed in the beaker with small portions of very dilute hydrochloric acid, 1 : 1000. Finally, the precipitate is brought on the filter. After drying at 100°, the salt is heated for some time at 145° or preferably the temperature is gradually raised until the precipitate just begins to sinter. The increase in weight is determined. Factor for Ag : 0.75273. See also p. 182.

DETERMINATION OF BISMUTH. GENERAL CONSIDERATIONS.

Bismuth is rather a rare metal, chiefly occuring in sulphidic ores and often in combination with antimony. To prepare a solution for the analysis, these minerals are generally dissolved in nitric acid. In the case of much lead being associated with bismuth, it is better to dissolve a portion in hydrochloric acid, though this will require more time. Otherwise much bismuth will be retained by the insoluble lead sulphate. If for some reason, nitric acid has to be taken for the decomposition, the residue is filtered off, the filter is freed from the precipitate as thoroughly as possible, then, it is incinerated separately at a low temperature. Filter ash and residue are fused with sodium carbonate, the cake is extracted with water to remove sulphate ion

and the decomposed melt is dissolved in dilute nitric acid; this liquid is added to the nitric acid solution of the sample.

Bismuth may be determined by hydrolysis of one of its salts. For a succesful operation according to this method, the absence of other elements which are easily hydrolized is required. It may also be precipitated with pyrogallol, oxine, cupferron and other organic reagents [197]. The best weighing form is the oxide, Bi_2O_3.

DETERMINATION OF BISMUTH. PROCEDURE.

The nitric acid solution is diluted to approx. 100 ml and dilute ammonia is added dropwise from a pipette with constant stirring and until a slight opalescence appears. If a precipitate is formed, this is collected, dissolved in nitric acid and the operation is repeated to remove traces of lead. The second precipitate is evaporated twice with nitric acid to remove hydrochloric acid. The impure nitrate is dissolved, the liquid is nearly neutralized with ammonium hydroxide as described above, then, after diluting to approx. 300 ml, the precipitation is completed with a *slight* excess of ammonium carbonate solution. The precipitate is digested on the water-bath for about two hours, is then filtered through a porcelain filter crucible and ignited to Bi_2O_3; in the beginning of this operation the temperature should be gradually increased to decompose the basic nitrate which is likely to be present. Weigh as bismuth trioxide; factor for Bi : 0.89704.

DETERMINATION OF LEAD. GENERAL CONSIDERATIONS.

Lead causes considerable trouble in analyses, unless when removed at the start. If it occurs together with silica, this constituent should be precipitated by evaporations with perchloric acid, see p. 140; lead is subsequently precipitated as sulphide. Natural sulphide minerals containing much lead, especially galena, are preferably decomposed with hydrochloric acid (the time required for the decomposition is increased by this alteration of the general procedure.) Otherwise the lead sulphate is partly deposited on fresh parts of the sample, thus preventing complete decomposition.

In the determination of lead, the co-precipitation of sulphates of the alkaline earth metals is avoided by a preliminary separation of the former element by electrolysis, lead peroxide being deposited on the anode, or by a separation with hydrogen sulphide. The electrolytic determination of lead is usually combined with the determination of copper, as the same conditions are required for both metals. Small amounts of lead may be weighed as peroxide. The precipitate retains some water [198]) and for larger percentages of lead this is chiefly a preliminary separation. The electrolytic method has been described in the section on the determination of copper, p. 225. Other methods for the determination of lead, viz. as lead molybdate, or as lead phosphate are of more restricted use [199]), whilst the titrimetric method generally is carried out after a preliminary separation of lead sulphate [200]).

DETERMINATION OF LEAD AS SULPHATE. PROCEDURE.

The solution containing not more than 0.5 g of lead is evaporated in a hot air bath with an excess of sulphuric acid until the residue is nearly dry. Repeat the operation with a few ml of sulphuric acid, 1 : 1, in the case that chlorides or nitrates were present in the original solution. Care should be taken in this operation to wash down the sides of the basin with water after every evaporation. The salts are digested with enough dilute sulphuric acid (1 % by volume) to dissolve sulphates of other metals and allowed to stand during a few hours. The employed acid should be preferably saturated with lead sulphate at room temperature. The precipitate is filtered off in a porcelain filter crucible and is adequately washed with dilute sulphuric acid, 1 : 100. Heat at approx. 500° in an hot air bath, electric oven, or other apparatus in which an oxidizing temperature can be maintained. Weigh as $PbSO_4$. Factor for PbO : 0.73606,
for Pb : 0.68334.

DETERMINATION OF COPPER. GENERAL CONSIDERATIONS.

After the elimination of silver, the arsenic group, bismuth and lead, only copper and cadmium remain in the solution, pro-

vided a preliminary separation with hydrogen sulphide has been carried out.

Electrolytic methods are best suited for the determination of copper. Lead peroxide is simultaneously deposited on the anode if this element has not been removed previously, see p. 223, this is an advantage in the case that minor percentages of lead are present and if this does not hold, a useful preliminary separation of lead is obtained. No contamination with cadmium need be feared.

Other methods for the determination of copper are less convenient to carry out; partly these are rather inaccurate, e.g. the cupro sulphide method [201]. The determination as cupro rhodanide and titrimetric procedures, however, are entirely satisfactory [202].

DETERMINATION OF COPPER. PROCEDURE OF ELECTROLYTIC METHOD.

Interfering substances are not likely to be present if the scheme of p. 220 has been followed. It is obvious that solutions, prepared in another way, should be free from metals which have a higher electrochemical potential than copper. Arsenic, antimony, selenium and tellurium must be avoided, as these would contaminate the deposited metal. The solution should not contain other acids than sulphuric or nitric acid and be free from oxidizing substances, especially dissolved oxides of nitrogen. The latter are formed in the solution during the electrolysis and their harmful effect should be neutralized by the addition of pure urea to the liquid [203].

Generally the electrolysis is done in a medium containing both nitric and sulphuric acids. Prepare a solution, containing approx. 4 % of concentrated sulphuric acid and 2 % of concentrated nitric acid by volume. A FRARY apparatus is preferably used. A current of 0.5 A is sufficient; a stronger current should be avoided, unless the solution is effectively stirred. At room temperature and without stirring, 6—8 hours are required. At approx. 70°, 100' are sufficient; the completeness of the precipitation is tested by adding some water to the solution. No new deposit should appear.

If lead is to be determined in the same liquid a sand blasted anode or another wire gauze electrode should be used. At first

the solution should contain some 10 % concentrated nitric acid by volume. In this phase lead (and manganese) are completely precipitated. After approx. 100', 10 ml of a 10 % urea solution in water are added [203]) followed by 100 ml hot water after another 30'. The further treatment of the electrodes has been described on p. 199. The anode with the deposited peroxide, however, should not be washed with alcohol, but dried at 160°.

The increase in weight of the cathode represents metallic copper. If the electrolytic determination of zinc is intended, the cathode should be reserved for this purpose, see p. 198.

The weight of PbO_2 on the anode is determined.

Factor for PbO : 0.93314,
for Pb : 0.86627.

Lead peroxide may be dissolved in nitric acid with the aid of some nitrous acid; this is conveniently obtained by placing some (e.g. electrolytic), copper in the liquid.

Determination of Copper as Cupro Sulphocyanate. Procedure.

Cupri salts are reduced by sulphurous acid. No more than 0.2 g of copper can be treated per 100 ml of solution, whereas up to 5 g with the electrolytic determination. Oxidizing substances, especially nitric acid should be absent. A neutral or feebly acid hydrochloric or sulphuric acid solution are suitable. This is easily obtained by nearly evaporating to dryness a solution containing a small excess of sulphuric acid and taking up the salts in slightly acidified water. This solution is treated at the temperature of the water-bath with an excess of sulphur dioxide solution. A saturated solution of sulphur dioxide is prepared, containing 3 % potassium rhodanide. A fivefold excess of this liquid is added to the copper solution, say 25 ml for every 0.1 g of copper. Several hours are required for a complete precipitation in an easily filterable form. Filter through a *porcelain* filter crucible, wash with cold water, containing some sulphur dioxide and then with a few small portions of cold water alone. Dry at 110—120° and weigh as CuCNS. Factor for Cu : 0.52272. The precipitate may be reduced to copper by heating it in a current of hydrogen (Rose cover and inlet tube). Alternatively, the cupro rhodanide may be dissolved and titrimetrically determined [204]).

DETERMINATION OF CADMIUM. GENERAL CONSIDERATIONS.

In the "filtrate" from copper, cadmium may be determined according to the procedure described on p. 155. As an alternative, this element may be separated as the metal, by electrolysis [205]). A sulphuric acid solution of cadmium is neutralized on phenolphthaleine with a pure sodium hydroxide solution, then a 10 % solution of sodium cyanide is added in *slight* excess over the volume required to dissolve the precipitate. Dilute to 100—150 ml and electrolyse with a current of 0.7—1.0 A at approx. 5 V. 5—7 hours are required for a complete precipitation. A sand blasted wire gauze electrode should be used. The further treatment as described in the general section on electro-analysis, see p. 199. The completeness of the precipitation may be tested with hydrogen sulphide. Only a very faint yellow colour should appear.

DETERMINATION OF ZINC. GENERAL CONSIDERATIONS.

Zinc is determined in the filtrate from the hydrogen sulphide group according to the procedure described on p. 155, or electrolytically. The latter method is almost exclusively applicable when a nearly pure solution of some zinc compound is investigated. The method is excellent for the analysis of alloys consisting essentially of copper and zinc. First, copper is deposited and weighed; then with the same electrode under changed conditions zinc is collected. A current of 0.5 A at 2.6 V is required in a solution containing 4 % of sulphuric acid.

Zinc can conveniently be precipitated in a mercury cathode with a current of 2—4 A at 6—10 V [206]). A strongly ammoniacal solution containing 5 g ammonium *nitrate* may be electrolysed with 0.4—0.8 A at approx. 6 V [207]). The results tend to be slightly high. In this latter process, chlorides should not be present in the solution, otherwise explosive NCl_3 may be formed.

DETERMINATION OF MERCURY. GENERAL CONSIDERATIONS.

Mercury is rather a rare metal. It occurs native and as the sulphide. Generally it is present only in traces in other minerals. The determination in mixtures is scarcely worth while conside-

ration as only deposits with high local concentrations have economical value. Mercury does not interfere in analyses for other constituents, as it is generally volatilized, either in the decomposition, or in the further treatments.

On this volatility are based the outstanding methods of determination, which will be briefly mentioned. Mercury is determined in a separate portion according to a docimastic method where it is volatilized by fusing the ore with lead chromate and adsorbed on a cooled piece of silver foil [208]. Or the decomposition is carried out in a way, similar to the PENFIELD method for the determination of water in rocks [209]. In this case, the ore is mixed with lead chromate and is covered in the tube also with a layer of lead chromate and in addition a layer of anhydrous sodium carbonate when chlorides are present in the sample. The various layers are separated with thin plugs of fibrous asbestos. To transfer the mercury vapours to the cool end of the tube, at the closed end a layer of magnesite is placed which on heating liberates CO_2. The tube is heated at first in the midst of it, where the pure lead chromate must be kept at a temperature of approx. 500°. Then, cautiously, the other parts of the tube towards the closed end are *gradually* heated. The mercury collects in the cool end of the tube. Finally this is separated from the heated part as in PENFIELD's method, dried cautiously and weighed *with* the mercury. After volatilization of the latter, the tube is again weighed and the difference is reported as mercury. For details, the reader is referred to the description of PENFIELD's method on p. 88 and to the original literature [209].

DETERMINATION OF MOLYBDENUM. GENERAL CONSIDERATIONS.

In the analysis of most substances, small amounts of molybdenum will be lost, except when a precipitation with hydrogen sulphide is carried out, and will not interfere with the determinations of other elements.

The most important ores are the sulphide and lead molybdate. Both ores yield easily to attack with acids. With sulphuric acid, lead is separated as sulphate and may be determined as described above.

Next arsenic is to be removed. This is effected by a precipitation of iron as hydroxide, arsenic being quantitatively carried down. A ten fold excess of iron is required, when necessary, this

is added as pure ammonium ferric alum. The solution is nearly neutralized with ammonia and the heated liquid is gradually stirred into a hot dilute ammonium hydroxide solution, 1 : 4. The precipitate is dissolved and reprecipitated in the same way. The filtrates are caught in one beaker, 2 g of tartaric acid are added to prevent co-precipitation of vanadium and tungsten, (see p. 215). The solution is saturated with hydrogen sulphide; the red thiomolybdate is formed but remains dissolved in the alkaline liquid. On acidifying with sulphuric acid, molybdenum trisulphide is precipitated. After standing overnight it is collected in a porcelain filter crucible, washed with dilute sulphuric acid containing some hydrogen sulphide, then with alcohol. After drying it is cautiously ignited to the oxide [210]).

Factor for Mo : 0.66667.

DECOMPOSITION OF ALLOYS. GENERAL CONSIDERATIONS.

Alloys containing silver, copper, nickel are dissolved in nitric acid. Aluminium alloys are more resistant to nitric acid than to hydrochloric acid. When copper and aluminium occur together the alloy should be decomposed with aqua regia. Light alloys are generally treated with hydrochloric acid. Alloys containing much aluminium and zinc may be often dissolved in concentrated solutions of alkali hydroxide. At the same time this is a preliminary separation of these metals from most others. Alloys containing considerable amounts of tin and antimony should be decomposed according to the methods prescribed for *ores* containing these metals. When only small amounts of these metals are present, a decomposition with nitric acid is often applicable, both metals remain undissolved as hydroxides and may be purified after a fusion with alkali polysulphide.

Often, fine shavings of alloys are prepared on the lathe. When these are submitted to an analysis, an extraction with ether, followed by washing with alcohol should be employed to free them from oil. Cf. p. 200.

OXIDE ORES. GENERAL CONSIDERATIONS.

A few ores of oxide character have not yet been considered: chromite, magnetite, titanite, manganese peroxide, pitchblende

and cassiterite. Except for chromium and uranium, gravimetric methods for the determination of elements occurring in these ores have been given. So, a few brief considerations are sufficient.

Chromite, titaniferous magnetite and titanite are very resistant to attack with acids. The latter two are easily decomposed — when finely divided — by fusing them with potassium pyrosulphate as described on p. 52 seq. Iron and titanium are determined according to the methods described on p. 46—60.

Manganese peroxide may be analysed according to one of the methods described, for the determination of manganese. The oxidizing power of this ore is often determined, as this largely determines the value for most purposes. In this case RUPP's method in phosphoric acid medium is preferable to BUNSEN's distillation process, as the latter has a tendency to yield low results [211].

Cassiterite is nearly insoluble in acids. It may be decomposed in a sulphurizing attack. Often it is more convenient to reduce the sample at higher temperatures in a current of hydrogen in a porcelain boat, introduced in a combustion tube [212]. Metallic tin results and can easily be dissolved in concentrated hydrochloric acid. The further treatment as described on p. 217 seq. For this attack the sample should be finely pulverized [212a].

In the next sections the analysis of chromite and pitchblende is briefly sketched.

ANALYSIS OF CHROMITE. PROCEDURE.

At most 0.25 g of the *finely powdered* ore is mixed with 3 g of sodium peroxide and fused in an iron crucible as described on p. 209 [213]. The melt is extracted with water and the liquid is saturated with carbon dioxide to precipitate most of the aluminium. The precipitate and residue are filtered off. The filter is ignited in the iron crucible. After complete incineration, the fusion with sodium peroxide is repeated. This melt is treated in the same way as described above; both filtrates are combined in a 600 ml beaker, nearly neutralized with nitric acid and evaporated in a porcelain dish. Any residual aluminium hydroxide is filtered off; then, the solution is slightly acidified. Chromium is precipitated as mercuro chromate, Hg_2CrO_4.

The solution containing the chromate is treated with a concentrated solution of mercuro nitrate and heated to boiling point. The precipitate can be easily filtered in a porcelain filter crucible; it is washed with a dilute solution of the precipitant.

The crucible is heated under a hood with vigorous draft, finally with the aid of a blast or in an electric oven. Weigh as Cr_2O_3.

Titrimetric procedures may be advantageously employed.

ANALYSIS OF PITCHBLENDE. PROCEDURE.

The determination of the uranium content is of interest because of the applications in the determination of the geological age of mineral deposits. In this case minute amounts of lead should be determined according to special procedures [214]).

Uranium belongs to the ammonium hydroxide group, but is not precipitated with cupferron when it is present in the sexivalent state. After reduction to the quadrivalent condition it is precipitated and may be determined as U_3O_8 [215]).

Dissolve the ore in concentrated nitric acid and filter off from insoluble parts. The filtrate in a porcelain dish is evaporated to fumes with a few ml of sulphuric acid and after dilution with water, this operation is repeated to remove nitric acid. Dilute again with water and precipitate the elements of the hydrogen sulphide group. In the filtrate, hydrogen sulphide is removed by heating on the waterbath. Finally, the solution is diluted to approx. 100 ml, 5 ml concentrated sulphuric acid are added and the metals are oxidized with a slight excess of permanganate solution.

Precipitate with cupferron in the cold solution as described on p. 58.

Wash the precipitate with 10 % sulphuric acid, containing 0.25 g cupferron per 100 ml.

The filtrate is evaporated to 50 ml and heated to strong fumes after the addition of 20 ml nitric acid. Repeat this with another 20 ml of nitric acid and finally with 10 ml water. Cupferron is destroyed by this operation.

The solution of the residue in 250 ml water is reduced with metallic zinc, e.g. in a JONES reductor (as, frequently employed for titrimetric procedures.) Add a slight excess of a 6 % cup-

ferron solution in water. U $(C_6H_5 N_2O_2)_4$ separates and is filtered off and washed as described above. Ignite filter and precipitate cautiously and weigh as U_3O_8.

The result may be checked according to titrimetric methods[215].

ORGANIC MINERALS AND ROCKS.

The most important substances belonging to this group are:

1. Peat — Lignite — Coal — Anthracite — Graphite — Diamond.
2. Mineral Oils — Asphalt — Fossil Resins, etc.

Part of the constituents in these materials is present in the form of organic compounds; other elements are exclusively present in inorganic matter; some divide.

Whilst most of the inorganic matter remains unchanged in the incineration, some alterations occur: 1. sulphides are oxidized, 2. iron II-oxide is oxidized to ferri oxide, 3. carbon dioxide resulting from the ignition may combine with insaturated metallic oxides, 4. silicates, primary and secundary carbonates and sulphates may undergo changes by double decomposition, 5. water is expelled. So, it is obvious that the ash-analysis of a sample does not represent the amounts of „inorganic" elements in the original substance. Besides the organic elements which are removed in the incineration, those inorganic elements which undergo changes, are to be determined according to special methods. These determinations, together with the ash analysis, enable us to give a discussion of the sample from the chemical point of view. Other, physical, values, however, are of interest for a *complete* discussion of the properties. For these physical determinations, as well as for the methods of preparing the sample, the special literature should be consulted [216].

Determination of Ash Content. Procedure.

A few gram of the sample is weighed out in a platinum or porcelain crucible or in a small dish of one of these materials. The heat should be very gradually raised; in the final ignition, the temperature must not be allowed to exceed 850°, otherwise

alkalies may be volatilized and the ash becomes insoluble in acids, (p. 149). Protect the contents of the crucible or basin against the flame gases by an asbestos shield, or by heating in a muffle. A distinction is made between "combined" ash and "free" ash. Their sum represents "total" ash. Combined ash is the ash of the pure organic parts and may be compared with the total ash of plants. The free ash results from mere mechanical contamination by parts of roof and floor and is consequently uninteresting from the scientific point of view, but all the more from the practical side.

The ash-percentage is calculated. Enough ash is prepared for the quantitative analysis (see p. 147, seq.) and the latter is carried out.

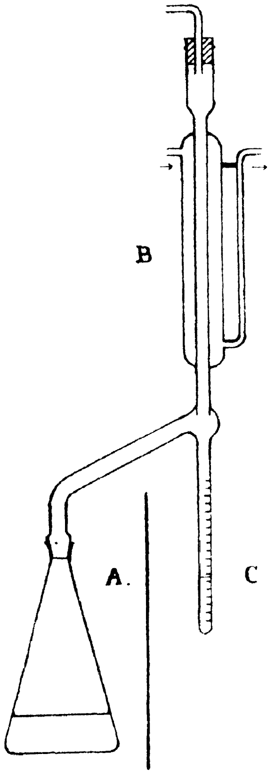

Fig. 16. Water determination with xylene distilling apparatus.

DETERMINATION OF WATER. PROCEDURE.

Water can be determined as loss in weight when the sample is heated at 105—110°, but this is not preferable as explained on p. 143 and altogether impossible with part of the substances here considered. A satisfactory process for the determination of H_2O— is the xylene distillation method [217]), see fig. 16. A suitable quantity of the sample is weighed out and is placed in the perfect dry Erlemeyer flask A of 500 ml capacity. Approx. 200 ml xylene, saturated with water at room temperature, are poured into the flask. A glass connection is made with a Liebig condenser B, fitted with a measuring tube C, (e.g. part of an old burette). Generally a few ml water should be placed in C, as in the lower part, the scale is either invisible or inaccurate. Proceed with the distillation until no more water collects in C. Calculate the percentage of water. This method may be employed likewise in other cases and it is best to have a permanent apparatus; if necessary two

or more condensers may be cooled with the same current of water.

DETERMINATION OF SULPHUR. PROCEDURE.

Sulphur may be present as sulphide, as sulphate and in organic compounds. To retain the organic and sulphide sulphur, the decomposition is carried out with 1 g of a specially prepared extra fine portion of the sample [218]). This is thoroughly mixed with twice the weight of ESCHKA mixture, (magnesium oxide: anhydrous sodium carbonate = 2 : 1) and placed in a porcelain crucible. The mixture is covered with 0.5 g of the "flux". The crucible is covered and placed in the hole of an asbestos shield to keep away flame gases. The temperature is very gradually raised; the mixture should not fuse or even sinter, as excessive quantities of silicates are decomposed then; this gives trouble, as silica is likely to contaminate the barium sulphate.

After complete oxidation of the organic matter (at the end of the decomposition this may be promoted by stirring with a nickel wire), the contents of the crucible are placed in a 600 ml beaker containing 200 ml water and a few ml of 30 % H_2O_2. Hydrochloric acid, 1 : 3, is added; sulphates are dissolved, sulphides are decomposed and oxidized. The liquid is boiled to completely dissolve the sulphur compounds and to remove carbon dioxide. After filtration, sulphur is determined in the filtrate as described on p. 99 and 162, seq. The required amount of barium chloride should be added in one pouring. If necessary, the barium sulphate may be purified by fusing it with sodium carbonate, followed by extraction of the melt. Factor for S : 0.13730.

A blank determination should be carried out with 10 g of the ESCHKA mixture and a corresponding correction applied in the actual determination.

In liquid organic deposits, sulphur should be determined according to CARIUS' method by a treatment as described on p. 210 for the analysis of pyrite.

DETERMINATION OF "ORGANIC" ELEMENTS. GENERAL CONSIDERATIONS.

The determination of C, H, N, and O may be carried out according to the well known methods of organic analysis or ac-

cording to the new procedures worked out by TER MEULEN[219]. Still other methods are available, among these, the method described by KJELDAHL for the determination of nitrogen is often employed and methods based on the process described by STREBINGER deserve more attention[220].

All these methods are extensively described in treatises of organic chemistry and are not given in this book, as the subject is of very restricted importance for the analysis of minerals and rocks.

Factor for H in H_2O : 0.11124,
C in CO_2 : 0.27277.

TABLE III. FACTORS.

Sought		Found		Factor	Log
Ag	107.880	AgBr	187.784	0.57449	.75928
		AgCl	143.324	0.75270	.87662
		AgI	234.777	0.45950	.66229
Al	26.961	Al_2O_3	101.926	0.52903	.72349
		$AlPO_4$	121.956	0.22107	.34453
		$Al(C_9H_6ON)_3$	458.936	0.05875	.76901
Al_2O_3	101.926	$AlPO_4$	121.956	0.41788	.62105
		$Al(C_9H_6ON)_3$	458.936	0.11105	.04552
As	74.899	Ag_3AsO_4	462.520	0.16194	.20936
		$Mg_2As_2O_7$	310.399	0.48260	.68359
As_2O_3	197.780	Ag_3AsO_4	462.520	0.21381	.33003
		$Mg_2As_2O_7$	310.399	0.63718	.80427
BaO	153.347	$BaSO_4$	233.386	0.65705	.81760
		$BaCrO_4$	253.336	0.60531	.78198
		$BaCO_3$	197.335	0.77709	.89047
Be	9.02	BeO	25.014	0.36060	.55703
		$Be_2P_2O_7$	192.003	0.09396	.97294
BeO	25.014	$Be_2P_2O_7$	192.003	0.26055	.41589
Bi	209.01	Bi_2O_3	466.000	0.89704	.95281
		BiOCl	260.449	0.80250	.90445
Br	79.901	AgBr	187.784	0.42549	.62889
C	11.999	CO_2	43.989	0.27277	.43580
Ca	40.070	CaO	56.067	0.71468	.85411
		$CaCO_3$	100.052	0.40049	.60259
		$CaC_2O_4.1\ H_2O$	146.045	0.27437	.43834
		$CaSO_4$	136.100	0.29442	.46897
CaO	56.067	$CaCO_3$	100.052	0.56038	.74848
		$CaC_2O_4.1\ H_2O$	146.045	0.38390	.58422
		$CaSO_4$	136.100	0.41195	.61485
$Ca_3(PO_4)_2$	310.170	CaO	56.067	1.8440	.26577
Cd	112.410	CdO	128.408	0.87541	.94221
		$CdSO_4$	208.435	0.53930	.73183
CdO	128.408	$CdSO_4$	208.435	0.61606	.78962
Cl	35.444	AgCl	143.324	0.24730	.39322
Co	58.940	CoO	74.936	0.78654	.89572
CoO	74.936	Co	58.940	1.2714	.10428

Sought		Found		Factor	Log
Cr	52.009	Cr_2O_3	152.005	0.68430	.83525
		$BaCrO_4$	253.336	0.20530	.31239
		$PbCrO_4$	323.208	0.16091	.20659
Cr_2O_3	152.005	$BaCrO_4$	253.336	0.30001	.47714
		$PbCrO_4$	323.208	0.23515	.37135
Cu	63.570	CuO	79.565	0.79897	.90253
		Cu_2S	159.187	0.79868	.90237
		CuCNS	121.614	0.52272	.71827
CuO	79.565	Cu	63.570	1.2516	.09747
		CuCNS	121.614	0.65424	.81573
F	18.993	CaF_2	78.059	0.48663	.68720
		PbClF	261.656	0.07259	.86088
Fe	55.840	Fe_2O_3	159.665	0.69946	.84477
FeO	71.833	Fe_2O_3	159.665	0.89980	.95415
Fe_2O_3	159.665	FeO	71.833	1.1113	.04585
H	1.001	H_2O	17.996	0.11125	.04630
I	126.900	AgI	234.777	0.54051	.73281
K	39.079	KCl	74.515	0.52444	.71970
		$KClO_4$	138.502	0.28215	.45048
		K_2O	94.155	0.83010	.91913
		K_2PtCl_6	486.063	0.16080	.20629
		$KClO_4$	174.192	0.44869	.65195
		Pt	195.245	0.40031	.60240
K_2O	94.155	K	39.079	1.2047	.07088
		KCl	74.515	0.63179	.80057
		$KClO_4$	138.502	0.33990	.53135
		K_2PtCl_6	486.063	0.19371	.28715
		K_2SO_4	174.192	0.54052	.73282
		Pt	195.245	0.48232	.68334
KCl	74.515	$KClO_4$	138.502	0.53801	.73079
		K_2PtCl_6	483.063	0.30661	.48658
		Pt	195.245	0.76330	.88270
Li	6.940	LiCl	42.377	0.16377	.21423
		Li_2O	29.875	0.46460	,66708
		Li_2SO_4	109.891	0.12631	.10143
Li_2O	29.875	LiCl	42.377	0.35249	.54715
		Li_2SO_4	109.891	0.27186	.43435
Mg	24.317	MgO	40.311	0.60323	.78048
		$Mg_2P_2O_7$	222.623	0.21846	.33937
		$Mg_2As_2O_7$	310.399	0.15668	.19501
		$Mg(C_9H_6ON)_2 . 2 H_2O$	348.295	0.06982	.84398

Sought		Found		Factor	Log
Mg	24.317	$Mg(C_9H_6ON)_2$	312.301	0.07786	.89131
MgO	40.311	$Mg_2P_2O_7$	222.623	0.36214	.55888
		$Mg_2As_2O_7$	310.399	0.25974	.41454
		$Mg(C_9H_6ON)_2 . 2 H_2O$	348.295	0.11574	.06348
		$Mg(C_9H_6ON)_2$	312.301	0.12908	.11086
Mg_2OCl_2	135.515	$Mg_2P_2O_7$	222.595	0.60880	.78447
Mn	54.928	MnO	70.922	0.77448	.88901
		MnO_2	86.920	0.63194	.80068
		$Mn_2P_2O_7$	283.825	0.38704	.58775
		$MnSO_4$	150.955	0.36387	.56095
MnO	70.922	$Mn_2P_2O_7$	283.825	0.49975	.69876
		$MnSO_4$	150.955	0.46983	.67194
$Mn_2P_2O_7$	283.825	MnO	70.922	2.00097	.30124
Mo	96.0	MoO_3	144.0	0.667	.82413
N	14.000	NH_3	17.003	0.82338	.91560
NO_3	61.985	NH_3	17.003	3.6455	.56176
		$C_{20}H_{16}N_4 . HNO_3$	374.982	0.16530	.21827
HNO_3	62.974	NH_3	17.003	3.7037	.56863
		$C_{20}H_{16}N_4 . HNO_3$	374.982	0.16794	.22515
N_2O_5	107.951	NH_3	17.003	3.1745	.50167
		$C_{20}H_{16}N_4 . HNO_3$	374.982	0.14394	.15818
Na	22.986	NaCl	58.428	0.39341	.59484
		Na_2O	61.975	0.74178	.87028
		Na_2SO_4	142.006	0.32373	.51018
		Na_2SiF_6	187.992	0.24454	.38835
		$(UO_2)_3MgNaAc_9 . 6 H_2O$	1497.141	0.01535	.18611*)
		$(UO_2)_3ZnNaAc_9 . 6 H_2O$	1538.201	0.01494	.17435*)
Na_2O	61.975	Na	22.986	1.3481	.12972
		NaCl	58.428	0.53032	.72454
		Na_2SO_4	142.006	0.43642	.63990
		Na_2SiF_6	187.992	0.32967	.51808
		$(UO_2)_3MgNaAc_9 . 6 H_2O$	1497.141	0.02070	.31597*)
		$(UO_2)_3ZnNaAc_9 . 6 H_2O$	1538.201	0.02014	.30406*)
NaCl	58.428	Na_2SO_4	142.006	0.82289	.91535
Ni	58.690	NiO	74.687	0.78581	.89532
		$NiC_8H_{14}O_4N_4$	288.676	0.20331	.30816
NiO	74.687	Ni	58.690	1.2726	.10468
		$NiC_8H_{14}C_4N_4$	288.676	0.25872	.41283

*) Ac = CH_3COO —

Sought		Found		Factor	Log
P	31.008	P_2O_5	141.987	0.43677	.64025
		$Mg_2P_2O_7$	222.595	0.27860	.44498
		$(NH_4)_3PO_4.12\ MoO_3$	1876.860	0.01652	.21801
		precipitate acc. to Lorenz		0.01439	.15806
P_2O_5	141.987	$Mg_2P_2O_7$	222.595	0.63787	.80473
		$(NH_4)_3PO_4.12\ MoO_3$	1876.860	0.03783	.57784
		precipitate acc. to Lorenz		0.03295	.51786
PO_4	94.988	$Mg_2P_2O_7$	222.595	0.85346	.93118
		$(NH_4)_3PO_4.12\ MoO_3$	1876.860	0.05061	.70424
		precipitate acc. to Lorenz		0.04409	.64434
Pb	207.232	PbO	223.221	0.92837	.96772
		PbO_2	239.219	0.86628	.93766
		$PbCrO_4$	323.208	0.64117	.80697
		$PbSO_4$	303.263	0.68334	.83463
PbO	223.221	Pb	207.232	1.0772	.03228
		PbO_2	239.219	0.93312	
		$PbSO_4$	303.263	0.73606	.86692
PbO_2	239.219	Pb	207.232	1.1544	.06234
S	32.045	SO_3	80.022	0.40045	.60255
		$BaSO_4$	233.386	0.13730	.13767
SO_3	80.022	$BaSO_4$	233.386	0.34287	.53513
		S	32.045	2.4975	
SO_4	96.017	$BaSO_4$	233.386	0.41141	.61427
Sb	121.755	Sb_2O_3	291.491	0.83539	.92189
		Sb_2S_3	339.654	0.71694	.85548
Sb_2O_3	291.491	Sb_2S_3	339.654	0.85820	.93359
Si	28.050	SiO_2	60.035	0.46723	.66953
Sn	118.700	SnO_2	150.694	0.78769	.89636
SnO	134.691	SnO_2	150.694	0.89380	.95124
Sr	87.620	SrO	103.616	0.84562	.92717
SrO	103.616	$Sr(NO_3)_2$	211.586	0.48971	.68994
		$SrSO_4$	183.657	0.56418	.75142
Ti	47.900	TiO_2	79.886	0.59960	.77786
U	238.320	U_3O_8	842.920	0.84819	.92850
UO_2	270.310	U_3O_8	842.920	0.96205	.98320
W	184.0	WO_3	232.0	0.7931	.89933

Sought		Found		Factor	Log
Zn	65.380	$ZnSO_4$	161.408	0.40506	.60752
ZnO	81.374	Zn	65.380	1.2446	.09504
		$ZnSO_4$	161.408	0.50415	.70256
Zr	91.220	ZrO_2	123.210	0.74036	.86945
		ZrP_2O_7	265.185	0.34399	.53655
ZrO_2	123.210	ZrP_2O_7	265.185	0.46462	.66710

The arrangement of this table is in the same form as in Chemisch Jaarboekje dl. II [10]), table 19. To obtain the mass of the constituent sought, multiply the mass of the substance found by the factor indicated in the third column.

The factors agree closely — not exactly — with those given in the text. In order to have mutual control, both series have been calculated from different data. This explains the slight divergences; the latter are altogether unimportant as compared with the experimental errors. The atomic, resp. molecularic weights have been calculated "in air", (cf. p. 9 and 12.), most of them by making use of the spec. gr. of the substance; in some cases, however, the molecularic weight in air has been obtained by the addition of the atomic weights in air, namely when the spec. gr. of the substance could not be used.

LIST OF APPARATUS.

Absorption apparatus for gases. Different types of U-tubes and GEISSLER-*bulbs* are required for the absorption of water vapour and carbon dioxide in the gravimetric determination of these constituents.

Asbestos shields. These and other wire gauzes should preferably be made of nichrome wire as these last longer and their initial higher cost is more than saved in the long run.

Aspirator. In gravimetric determinations of water and carbon dioxide an aspirator will yield good service. This apparatus may be substituted by an ordinary wash bottle. The short tube of the bottle is fitted with a piece of rubber tubing and a clamp or cock. The bottle is clamped in a reversed position in a stand. Instead of these apparatus, the suction pump may be used, provided a large empty bottle is placed between pump and absorption tubes to level the irregularities caused by the variations of the water pressure.

Balance. Any "analytical balance" of a quality make can be used. A capacity of 200 g and a sensitivity of 0.1 mg at *full* capacity are required. Further information on this subject will be found in the section "Weighing" on p. 25 and in the "Instructions for Use" supplied by the manufacturers.

Basin. A platinum basin of not too small capacity (300—400 ml) is very valuable in silicate analysis and occasionally, larger basins may be used with much profit. It is advisable to have at hand smaller basins of 100, 50 and 25 ml capacity to serve in decompositions for the alkalies, phosphorus, manganese, etc.

Beakers. The ordinary GRIFFIN form of beaker in different sizes from 50—1000 ml capacity is most convenient for almost every purpose. The interior surface should be unscratched and smooth as some precipitates have a tendency to adhere at raw surfaces. Beakers, like other glass apparatus, should

be made of resistance glass. Jena, Jena-Duran and Pyrex glass are well suited for general chemical work.

Blast. A blast burner is required for glass blowing and for the ignition of some precipitates, especially Al_2O_3. In most other cases a MEKER burner is more convenient.

Bottles. Reagent bottles for liquids should be made of resistance glass and should have caps (f.e. old beakers) to protect the stopper and neck against dust. Whenever possible, the solid reagents should be used and dissolved as needed. Reagents of analytical quality are now sold in very convenient glass bottles with bakelite stoppers, a decided improvement.

Burette. Though weight burettes have slight advantages as to accuracy of reading, they are generally not required for ordinary analyses and to some degree they are even inconsistent with the character of titrimetric analysis. For most work the ordinary form of the MOHR burette with some device to secure readings without parallaxis errors is entirely satisfactory.

Burners. Besides a blast, one or two MEKER burners and a number of ordinary BUNSEN burners are required.

Centrifuge. A small centrifuge is valuable for mineral separations and for microchemical work.

Clock glasses. Watch- or clock glasses are required in different sizes as a cover for beakers and dishes. They should be made of resistance glass.

Colorimeter. Refer to section "Colorimetry", p. 27 seq.

Combustion tubes.

Condensers.

Crucibles.

Platinum: When economy with platinum is necessary, two crucibles, one of 20 ml and one of 25 ml capacity are most generally applicable. For the decomposition of the portion wherein ferrous iron is to be determined, a crucible of 40 ml is desirable, this crucible will serve also in the determination of the alkalies for the decomposition when a finger crucible is not available and for the final evaporation of the mixed chlorides. For fusions, a crucible of 25 ml cap. is required, but this crucible may advantageously be made of palau, (see there). A finger crucible of platinum is very convenient for the decomposition according to LAWRENCE SMITH (p. 72, seq.) but can not be used for other purposes. A number of smaller crucibles of 15 and 10 ml capacity

can be used in ignitions of smaller precipitates. Every crucible should have its own cover; except for fusions, the closer fitting covers with a small button are preferable to the flat model. Platinum crucibles and other apparatus are readily attacked by halogens and, when hot, by alkali hydroxides, sulphides, arsenides, antimonides, phosphides, sulphur, phosphorus, heavy metals, lithium compounds, burning carbon and non-oxidising flame gases. Consequently these substances are to be avoided as well as other materials which are likely to liberate them. Filter papers should be carbonized at a very low temperature and the carbon burnt off without visible flame. The non-luminous flame of gas burners should always be used to heat platinum apparatus and the inner cone of the flame must not be allowed to reach the platinum. Platinum apparatus should be kept clean by rubbing them with "soft" sand with rounded-off corners (sea-sand f.e.) or by fusions with borax or potassium pyrosulphate. Excessive temperature changes should also be avoided.

The use of platinum GOOCH or NEUBAUER crucibles is not recommended because of their high cost and the rather severe precautions which are necessary in their use.

Palau: This alloy contains 80 % pure gold and 20 % palladium and has many advantages for fusions with alkali carbonates or hydroxides as it is much less attacked than platinum and in most cases the melt is easily loosened from the crucible. The alloy can safely be heated up to 1200°. So, a *powerful* blast should not be used, but this is never required in fusions.

Gold. This metal can be used in fusions with alkali hydroxides but has no advantages over palau.

Silver. A silver crucible with heavy walls can be used in fusions with alkali hydroxides except in very accurate work.

Nickel. The same may be said on the use of nickel crucibles. Larger nickel crucibles can be used as a radiator by placing a triangle in them. Another, smaller crucible can be placed free in the radiator and be equably heated over the whole surface, e.g. in evaporations of sulphuric acid, fusions with potassium pyrosulphate and ignitions in the presence of organic matter.

I r o n. Iron crucibles are required for fusions with sodium peroxide and may also serve as radiators. A finger crucible of sheet iron may be used as substitute for one of platinum.

P o r c e l a i n. Porcelain crucibles are often used for operations with substances which would damage platinum crucibles. Porcelain filter crucibles have very fine pores (to 0.75 mu) and retain the finest precipitates. They should be heated with a crucible cap over the bottom, which otherwise will crack on heating. One ROSE crucible with cover and inlet tube should be available.

G l a s s. For the use of glass filter crucibles, see p. 21.

F u s e d s i l i c a: Crucibles of fused silica may substitute platinum crucibles in some cases, e.g. in the ignition of magnesium pyrophosphate.

Crucible tongs. A pair of BLAIR's crucible tongs should be used to handle hot platinum crucibles: a pair of straight ordinary tongs is fitted with platinum shoes and rather long stiff platinum wires, bent in a half circular form. This is the only apparatus which enables the chemist to handle crucibles in a safe way and without removing the cover.

A pair of crucible tongs with platinum shoes of ordinary form is still more required.

Decantation flask. A very convenient model made of Jena glass, cf. fig. 10, p. 131.

Dessicators. A larger dessicator is used to keep special reagents in a perfect dry condition. Two 12 or 15 cm dessicators are used to cool ignited crucibles in the absence of moisture and carbon dioxide. One of these should contain calcium chloride as active agent, the other pieces of sodium hydroxide.

Distillation apparatus for acids and ammonia. A simple apparatus consisting of a retort with side tube, condenser, inlet tube and receiver will serve very well. The retort is heated with a toadstool burner.

Distillation flasks.

Dishes. Platinum: cf. Basin.

Fused silica: A dish of this material, capacity approx. 400 ml is required in the determination of silica, a smaller of 150—200 ml cap. is useful to disintegrate the fusion cake obtained in the decomposition according to LAWRENCE SMITH. One of 15—20 ml cap. should be reserved for the determination of potassium in the mixed alkali chlorides.

Porcelain: dishes in various sizes are required e.g. from 5—15 cm diameter.

Electric oven. This instrument as well as electric hot plates and furnaces will facilitate the work of the chemist considerably. For evaporations in crucibles or small dishes, electric cigar lightners are unsurpassed.

Electrolyse apparatus. Cf. the description on p. 197, seq.

Erlemeyer Flasks in different sizes from 50—500 ml capacity.

Filtration, required apparatus cf. p. 18, seq.

Flame screens. Two entirely different forms are required. The first form protects the flame against draughts: a sheet iron cap fixed on the chimney of the burner; the second form is a shield of asbestos or better of platinum foil with an opening to place a crucible and serves to protect the contents of the crucible against flame gases.

Flasks. Erlemeyers, flat-bottom, round-bottom and distillation flasks in various sizes should be at hand.

Funnels. Glass funnels: see p. 20. A small funnel made of platinum or hard rubber should be available for work with HF.

Funnel supports. Both metal and wooden funnel supports have decided disadvantages. The following resolution has proved to be entirely satisfactory: cut off the rings and the largest part of the arms of a three arm metal funnel support and slip pieces of thin rubber tubing over the remaining parts. The removed parts are copied in glass tubing of a width which will fit the rubber tubing and these are put in place. These supports are easily cleaned and the chance of contamination of the liquid in the beaker is reduced to the minimum.

Glass. Glass tubing in various widths are required to make connections etc. Jena, Pyrex or other resistance glasses are far preferable to ordinary glass. Glass rods are required to prepare stirring rods and supports of every kind. In the former case the diameter should not be more than 3 mm.

Hammer. A so-called geological hammer is most useful in the preparation of the sample.

Hot air bath. Nickel, iron and other crucibles may serve as hot air baths or radiators. With electric apparatus very convenient radiators can be made. To concentrate or evaporate solutions in crucibles I have found electric cigar lightners most convenient. Two lightners are connected in series, other-

wise the temperature will rise too high and the filaments are likely to burn on quickly.

Kipp Apparatus. For small scale experiments the handy Kipp-apparatus may be used to prepare gases like carbon dioxide, hydrogen and hydrogen sulphide.

Kjeldahl flasks. Besides for the determination of nitrogen in organic substances according to KJELDAHL, these flasks can be used with much advantage for other decompositions.

Magnifying glasses.

Mortars. A diamond mortar is required to reduce fragments of minerals and rocks to such a powder as can conveniently be treated in an ordinary agate mortar. The composition of the special hard steel used for this mortar should be known when spectrographic investigations for traces of rare metals are intended. In general it is advisable to prepare a sample for the chemical investigation, then proceeding directly with the preparation of a sample for the spectrographic analysis, using only the agate mortar for this part of the work.

An agate mortar of at least 6 cm is required to reduce the powder of rocks, minerals, etc. to the degree of fineness, required for the decomposition.

A porcelain mortar of large size, (10—15 cm diameter) is required to pulverize chemicals.

Nessler tubes. See p. 29.

Oven. As recommended by OUDEMANS (Z. anal. Chem. **11**, (1872), 289) an oven with transparent mica walls is preferable.

An electric oven serves admirable for fusions and ignitions.

Pipettes.

Platinum. Platinum wires of 0.8—1.0 mm thickness are required to stir solutions containing hydrofluoric acid. A platinum cone with fine openings is used for filtrations under suction with filter paper. For preparative work, a BUECHNER funnel can be used with much advantage.

Pump. A suction pump and a compressor are required in the laboratory. There are several types which all meet more or less satisfactory the demands of analytical work.

Radiator: See Hot air bath and Crucible, iron.

Rubber tipped glass rod. This may be made of a piece of rubber tubing slipped over a somewhat thicker glass rod, but the author has found the following form which can easily be prepared in the laboratory preferable: a rubber stopper is

cut off on two sides so that the form of a wedge of WALLIS is obtained. In the midst of the circular basis, a hole is bored to fit a glass rod.

Sample tubes. Larger and smaller labelled tubes with cork and rubber stoppers.

Sieves. In the preparation of samples, sieves are used to avoid the formation of too many dusty particles. These sieves should be free from elements which are present only in minor percentages and will nevertheless be investigated, c.q., a special portion of the sample is prepared without the use of these sieves. Cf. also: Mortar, diamond mortar.

Spatula. Spatula's made of nickel, platinum and V_2A-steel may be used with much advantage now and then, though those of horn and porcelain are most often used.

Ring stand. Ring stands with heavy bases and adjustable height are required in various sizes. These should preferably be made of non-corrosive steel, but ordinary iron stands may be used, especially when painted with aluminium paint. It is advisable to place a somewhat wider piece of glass tubing on the higher, projecting end to avoid contamination by pieces of the surface of the bar.

Rubber stoppers. These should be free from antimony and in special cases the absence of still other elements should be secured.

Still. It is most convenient and safe to prepare distilled water in the laboratory as needed.

Stirring rods. These should be made of thin glass rods, approximately 3 mm thick. The ends are rounded off in the flame. Thicker rods are not required and are more likely to scratch beakers.

Thermometers. For temperature measurements in distillations, in ovens and other apparatus and for other purposes two or three thermometers are required, e.g. 0—110°, 0—160° and 0—360°.

Toadstool. To avoid spluttering when heating liquids in a flask, a toadstool model glass cover may be used: p. 175, fig. 11b; p. 177, [130]).

Triangles. For platinum crucibles, triangles of platinum are superior to all others, though nichrome wire does not alloy appreciably with platinum. Fused quartz does not keep as well here as in most other apparatus, a good quality unglazed

porcelain is much better. Pipe-clay triangles are generally very bad.

U-tubes: Cf. absorption apparatus for gases.

Wash-bottles. Wash-bottles are required for wash-liquids which are often used e.g. cold water, hot water, dilute hydrochloric acid, dilute ammonia etc. The rubber balloon of the convenient type of balloon wash bottles should be perforated at the equator. The top of one of the fingers is placed on the small hole when the bottle is in use. This hole prevents dropping of liquids as a result of temperature or pressure changes, the balloon is easily cleaned and the bottle may conveniently be filled by placing the outflow opening under the surface of the liquid, contained in a flat dish and applying suction through the hole.

Watch-glasses: cf. Clock glasses.

Water-baths: with overflow and concentric *porcelain* rings.

Weights: cf. p. 25 seq. For most work, brass gram weights and nickel mg weights are satisfactory. The atomic and molecularic weights and the factors given in this book have been calculated for this case. In general, these factors may be used for other combinations, but when the utmost accuracy is required, the correction for buoyancy should be applied on the international atomic weights, etc.

Wire gauze. Nichrome wire gauzes should be used throughout. Cf. Asbestos shield.

LIST OF REAGENTS.

The utmost care should be taken in purchasing and testing chemicals for analytical work. The best quality should be used throughout; nevertheless, corrections for impurities are often required as enormous amounts of reagents are used in the course of more complex analyses. The numerical value of these corrections should be ascertained under conditions most closely resembling the experimental conditions of the analysis, cf. p. 31. This value should be marked on the label of the bottle.

Acetic acid.

Alcohol. Methyl, ethyl, normal butyl, iso-butyl and amyl alcohol. All of these will occasionally find application, especially in separations of the alkalies and alkaline earth metals. Ethyl alcohol of sp. gr. 0.81 as required in the separation of K and Na (p. 81) is obtained by mixing 5 vol. of 96 % alcohol with 1 vol. of distilled water.

Ammonia. This reagent is often very impure, especially when it has been stored for some length of time in glass bottles. Ammonia water is most conveniently prepared by introducing the gas from a cylinder through distilled water in a ceresine bottle. The gas is also obtained by heating concentrated ammonia water (25 %). For several reasons it is advisible to prepare every week a fresh quantity of the reagent. It is most important to secure that carbonate is absent (otherwise the sesquioxide precipitate will be contaminated by earth alkalies) and that on evaporation no solid residue remains.

Ammonium acetate.

Ammonium carbonate should be wholely volatile. The solution should be prepared as needed by dissolving the powdered salt in *cold* distilled water.

Ammonium chloride is often used to give a buffering action.

A concentrated solution is prepared by just neutralising pure conc. HCl with fresh ammonia water.

Ammonium dichromate. This should be free from sulphuric acid to serve in the determination of barium, (p. 159).

Ammonium molybdate reagent. 30 g of the pulverized salt are dissolved in 500 ml water whilst constantly stirring.

Ammonium nitrate. A solution of one part of the salt to three parts of water is required in the determination of phosphorus as phosphomolybdate. A 2 % solution is often used as wash liquid e.g. for the ammonia precipitate. This solution should be carefully neutralized with ammonia as the solid salt often contains an excess of nitric acid.

Ammonium oxalate. The solid salt should be dissolved as needed; a small volume of hot water is sufficient for a few gram. A 1 % solution may be kept in a ceresine bottle or a glass bottle with a thick interior coating of ceresine.

Ammonium rhodanide.

Ammonium sulphate.

Amyl alcohol.

Aqua regia. 1 vol. of HNO_3 is mixed with 3 vol. of conc. HCl as needed.

Arnd's alloy. 60 % Cu — 40 % Mg.

Asbestos.

Ascarite or *Soda-asbestos.* Asbestos fibres are impregnated with sodium hydroxide. The preparation is tedious and in most cases, finely pulverized sodium hydroxide is far to be preferred for its greater capacity of absorption.

Barium chloride. A 10 % solution in water is to be prepared.

Barium hydroxide. This is required in the modified Berzelius method for the determination of the alkalies, (p. 193).

Borax.

Boric acid. A saturated solution in water is prepared.

Bromine. Bromine water is prepared as needed or may be kept as a saturated solution. Bromine often contains chlorine and should in this case be distilled with pulverized KBr.

Bromoform.

Cadmium acetate.

Calcium carbonate. Specially prepared calcium carbonate is used in the determination of the alkalies according to L. SMITH. The flux is weighed to 0.1 g and an appropriate portion is treated as in the procedure for the determination of sodium.

In general, potassium may be safely assumed to be absent, a spectroscopic test is in place here. Stocks containing more than 0.5 at most 1.0 mg alkali chloride should be thoroughly washed with several portions of hot water or be purified by dissolving the carbonate in pure HCl, followed by re-precipitation for not more than two thirds of the amount present with pure ammonium carbonate at a temperature of 80 °. The precipitate is thoroughly washed with hot distilled water.

Calcium chloride. For use as dessicant, the granular — not the fused — form is required. When CO_2 is also to be determined in a current of gas, the calcium chloride should be carefully neutralized by replacing the air in the container by carbon dioxide. The salt is kept overnight in this atmosphere under the pressure of a Kipp-generator. Then, any carbon dioxide is to be removed by applying various times a vacuum with the aid of a suction pump.

Calcium fluoride. Pulverized fluorspar is used in a qualitative test for boron, (p. 114).

Calcium oxide is used in some variants of the BERZELIUS method for the determination of sodium and potassium and is prepared by heating a few g of the carbonate from the stock for the L. SMITH method.

Carbon dioxide. A Kipp- or other generator may be used or preferably a cylinder with the liquefied gas. The gas should be washed with copper sulphate solution to retain H_2S and with water to retain HCl.

Carbon tetrachloride.

Chloroplatinic acid. A solution is prepared containing 1 g Pt / 10 ml.

Citric acid. A 10 % solution is required in the determination of phosphorus. A weaker solution is often used to prepare soil extracts.

Copper sulphate.

Cupferron. The ammonium salt of nitrosophenylhydroxylamine may be used with much advantage in quantitative analysis, especially for the determination of Ti, Zr, Sn, U and other elements. It is a very bad skin poison and should be handled with care.

Devarda's alloy. 50 % Cu — 45 % Al — 5 % Zn.

Diacetyldioxime. A 1 % alcoholic solution is made up as needed.

Diammonium hydrogen phosphate. This salt is preferable to the sodium compound.

Diphenylamine. A 0.2 % solution in sulphuric acid is used as an indicator in oxydation-reduction processes.

Disodium hydrogen phosphate.

Ether. In quantitative analysis ether is often used for extractions, e.g. in the alkalie and alkaline earth group and for iron III-chloride in acid medium.

Ferric sulphate, free from halogens.

Ferrous sulphate, free from arsenic.

Filter paper. Quantitative filters should be used for most analytical purposes as their ash-content can generally be neglected in ignitions. Good quality filters are now sold in cardboard boxes and should be kept in these to protect them against dust. The filter pulp used in their preparation should be extracted with hydrofluoric and hydrochloric acids. The sizes from 5.5—12.5 cm should be at hand.

Filter paper pulp. Tablets of easily "soluble" filter paper pulp can now be obtained (Schleicher and Schüll, f.e.). When prepared in the laboratory, a few large size filters are teared up and the fibres loosened by vigorously shaking the pieces with water. Concentrated acids should not be used, as organic products are formed which will interfere in several determinations. Cf. p. 21.

Glycerol is used in the titration of boric acid if mannite is not at hand. Consequently, commercial glycerine to be used for this purpose should be carefully neutralized with dilute sodium hydroxide solution as it often contains organic acids.

Hydrazine sulphate.

Hydrochloric acid. The purest hydrochloric acid should be used throughout. If not obtainable at reasonable price the reagent may be prepared in the laboratory in the same way as ammonia, viz. by heating the the 38 % acid and dissolving the escaping vapours in distilled water.

Hydrochloric acid gas is prepared by dropping concentrated sulphuric acid on a mixture of NaCl and HCl in a gas evolution apparatus.

Hydrofluoric acid. This should be handled with care as it causes dangerous burns on the skin. On evaporation no solid matter should remain. This is best secured by obtaining and keeping the reagent in ceresine bottles.

Hydrogen. Preferably a cylinder with the gas should be used. For smaller laboratories a Kipp apparatus will serve as well, especially when the modified form is used: F. HENZ — Chem.-Ztg. **26**, (1902), 386.

Hydrogen peroxide. Fluorine, sulphuric acid organic stabilizing agents should be absent. For some purpose, there should remain only a negligible amount of solid matter on evaporation. It is best to keep this reagent in paraffinated bottles as sold by Merck f.e., (perhydrol).

Hydrogen sulphide gas should be washed with water.

Hydrobromic acid.

Hydroiodic acid.

8-Hydroxyquinoleine. A 5 % solution in 2 N. acetic acid is prepared and should be kept in the dark.

Indicators. For general analytical work the following solutions are most useful:

Dimethyl yellow: 0.1 % in 90 % aethanol,
Methyl orange: 0.1 % in water,
Congo red: 0.1 % in water,
Methyl red: 0.1 % in 60 % aethanol,
Para nitrophenol: 0.2 % in water,
Phenolphthaleine: 1.0 % in 60 % aethanol.

Iron sulphide.

Lead acetate paper.

Lead chromate.

Lead oxide and lead peroxide as used for elementary analysis according to DENNSTEDT.

Macerated filter paper; see: Filter paper pulp.

Magnesia mixture. As recommended by HILLEBRAND an acid chloride solution should be used: "dissolve" 50 g $MgCl_2 . 6 H_2O$ and 100 g NH_4Cl in 500 ml water. Add ammonium hydroxide in slight excess, let stand overnight and filter if a precipitate appears. Make just acid with hydrochloric acid, dilute to one liter and keep in a glass-stoppered bottle. (HILLEBRAND-LUNDELL — 1929, p. 39).

Manganous sulphate.

Mannite.

Mercuric chloride.

Mercuric oxide.

Mercuro nitrate.

Mercury.

Nitrid acid. The fuming nitric acid should be available to prepare an acid of density 1.44—1.46 as required in the determination of Sr, p. 67. It is advisable to prepare other dilutions with 65 % acid (d. 1.40). Fuming nitric acid cannot be diluted with water, the concentrated acid (65 %) should be used instead.

Nitron acetate. A solution of the reagent is used containing 10 g in 100 ml of 5 % acetic acid in water. The reagent should be kept in the dark.

Oxalic acid.

Oxine, See : 8—Hydroxyquinoleine.

Perchloric acid.

Phenylhydrazine.

Phosphoric acid. Syrupy phosphoric acid (d = 1.70, appr. 83 %) is used for the determination of CO_2 and C according to DIXON, (p. 130).

Phosphorous acid.

Potassium arsenate, pure primary, (KH_2AsO_4).

Potassium biiodate.

Potassium bromide.

Potassium cyanide.

Potassium dichromate.

Potassium carbonate, free from sulphate and phosphate.

Potassium periodate.

Potassium permanganate.

Potassium persulphate.

Potassium pyrosulphate.

Potassium rhodanide. A 3 % solution in water, saturated with SO_2 is used in the gravimetric determination of copper, (p. 226).

Potassium sulphate.

Pumice, impregnated with anhydrous copper sulphate. 0.5 cm size fragments of pumice (without dust) with half their weight of copper sulphate as a concentrated solution are evaporated to apparent dryness, whilst constantly stirring and are then kept for 3—4 hours in an air bath at 160°.

Potassium nitrate.

Silver foil.

Silver nitrate.

Silver sulphate.

Soda lime.

Sodium carbonate.
Sodium hydroxide.
Sodium nitrate.
Sodium nitrite.
Sodium oxalate.
Sodium peroxide.
Sodium sulphide.
Sodium sulphite.
Sodium thiosulphate.
Standard solutions.

Chromium: dissolve 0.2554 g K_2CrO_4 to one l. Chromium content : 0.1 mg Cr_2O_3 ml.

Manganese: dissolve 0.2228 g pure dry potassium permanganate in approx. 700 ml water, add 25 ml sulphuric acid and decolorize just with sulphur dioxide water. After cooling dilute to 1 l. 0.1 mg MnO / ml.

Permanganate: dissolve approx. 1 g of the pure salt in water to 1000 ml and keep for an hour at boiling temperature. Filter through a glass filtering crucible into a dark bottle. Standardize with oxalic acid or sodium oxalate. 1 ml of this solution is equivalent to approx. 0.00225 g FeO or 0.0025 g Fe_2O_3. Keep the solution protected against direct daylight by placing it in the dark and against dust by a cap on the bottle. *)

Titanium: Ignite 0.2—0.3 TiO_2 over a blast and weigh exactly. Fuse with potassium pyrosulphate as described on p. 52 until a clear melt results. Dissolve in 10 % sulphuric acid, making the volume up to one liter. Standardize exactly by treating 50 ml portions of this solution as described on p. 58, (THORNTON's method).

Sulphur. For the Freiberger attack purified sulphur should be used (re-crystallized from CS_2).
Sulphuric acid.
Tartaric acid.
Titanium dioxide.
Uranyl reagent. This reagent for the determination of sodium is prepared by dissolving 32 g crystalline uranyl acetate and

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*) $COOH.COOH + O \rightarrow 2\,CO_2 + H_2O$ COONa . COONa
$2\,FeO + O \rightarrow Fe_2O_3$
$2\,FeO : COOH.COOH = 1.5966.$
$2\,FeO : COONa.COONa = 1.0725.$

100 g magnesium acetate in a mixture of 20 ml acetic acid, 500 ml ethyl alcohol and 300 ml water. This is aided by heating on the water-bath. After cooling, the volume is made up to 1000 ml with water and after some days the precipitated sodium salt is filtered off (this results from contamination of the reagents with sodium). The liquid will now be saturated with the precipitate at room temperature and is ready for use at the same temperature. Keep in the dark.

Water. Water should be distilled at short intervals and be used as fresh as possible. To remove the largest part of dissolved carbon dioxide it may be aerated.

Xylene. Pure xylene of boiling point 138-139-145° is saturated with water at room-temperature to serve in the water determination according to the xylene distillation method, p. 234.

Zinc. Zinc powder and granulated zinc are used for reductions. Very pure zinc can be activated with a few drops of copper sulphate or platinum chloride solution.

Zinc oxide.

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› reference has been given to the parts:
list of apparatus
list of reagents
these are arranged in alphabetical order of subjects.

anal. = analysis, analyses,
det. = determination,
sep. = separation.

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